Transport Behavior of Oil in Mixed Wettability Shale Nanopores

Guoxiang Zhao,* Yuedong Yao, Caspar Daniel Adenutsi, Xiaolong Feng, Lian Wang, and Wenwei Wu

ABSTRACT: Shale oil reserves play an important role in the oil & gas industry. The investigation of oil transport behavior in shale nanopores is crucial in the successful exploitation of shale oil reservoirs. However, the transport mechanisms of oil in shale nanopores are still not understood. In this paper, a model for oil transport through a single nanopore was established by considering mixed wettability, surface roughness, varying viscosity, and the effects triggered by adsorbed organic matter. The organic surface ratio of a single nanopore was used to quantify mixed wettability, while the effects of adsorbed organic matter were estimated by the surface coverage and the adsorption thickness. The entire mathematical model was simplified into several equations to discuss the contributions of each mechanism. The results showed that to accurately predict the oil transport properties in mixed wettability shale nanopores, it is necessary to consider varying viscosity, wettability alteration, and the oil molecule structure. Adsorbed organic matter led to increase in oil wettability shale nanopores, it is necessary to consider varying viscosity, wettability alteration, and the oil molecule structure.

1. INTRODUCTION

As the gap between the world’s energy supply and demand continues to increase, exploration and development of unconventional resources have become a new target.¹⁻⁴ Unconventional resources mainly include heavy oil, low permeability reservoirs, and oil shale reservoirs. Among these unconventional resources, shale oil has abundant reserves and is gradually serving as one of the main replacements for conventional energy supplies.⁵⁻⁸ In recent times, several researches have been carried out to study oil flow mechanisms in shale nanopores.¹⁻⁴,⁶⁻¹³ However, due to the ultra-low permeability and widely distributed disconnected organic nanopores, the development of shale oil reservoirs has a lot of challenges.¹⁴⁻¹⁷ On one hand, the properties of nanopores are complex and diverse. Moreover, nanopores are composed of organic and inorganic surfaces. Additionally, the pore surface is rough with heterogeneous wettability.¹⁸⁻²¹ On the other hand, crude oil has complicated composition (n-alkanes with different chain lengths, resins, and asphaltenes) and organic matter, which some studies reported as causes of formation damage.⁵,²⁰⁻²⁴ It is therefore necessary to consider these factors in order to understand oil flow mechanisms in shale rocks.

Given the fact that the components of crude oil are complex and complete organic particle is difficult to obtain from shale rocks, knowledge about oil transport mechanisms in organic pores is still limited and hardly explored experimentally.²⁵,²⁶ As a result, the molecular dynamics (MD) simulation method was widely adopted in some previous researches.²⁷⁻³⁰ In these studies, organic matter is usually simplified to graphene. Primary MD simulation studies²¹ reported static adsorption of organic matter and dynamic flow behavior of shale oil. Besides, the mass transport rate of oil in organic nanopores is of 1⁻³ orders magnitude greater than that predicted by the no-slip Poiseuille law. This is also called flow enhancement phenomenon. The phenomenon can be attributed to the slip flow in the surface of a nanopore and the layering structure of oil near the pore surface.²³⁻²⁵,²⁷ MD simulations²⁸ showed that liquid⁻liquid slip is non-negligible when oil flows in hydrophilic quartz nanopores in the presence of a thin water film. In other words, the water film may be regarded as a special inorganic subsurface with a certain degree of mobility. Results showed the distinct flow capacities of organic and inorganic surfaces.
nanopores in that oil flow in organic pores is faster.\textsuperscript{20,22,31} Although the MD simulation method can simulate liquid flow behaviors in nanopores under some conditions, it is time-consuming and difficult to use in describing the interfacial dynamics, mixed wettability, and pore surface roughness and to quantify adsorption of organic matter.\textsuperscript{1} Moreover, there is a significant error in the estimation of the overall flux if these factors are ignored. Additionally, although an empirical formula can be obtained by MD simulation, it cannot reveal oil–pore wall interaction mechanisms and oil transport behaviors in nanopores.\textsuperscript{31,38,39} In addition, physical quantities such as slip length and viscosity of oil in the interfacial region needs to be formulated to characterize the real interaction between oil molecules and pore surface. In fact, due to the strong interplay between oil molecules and pore surfaces, the viscosity of the interfacial region oil is significantly larger than that at the macroscale.\textsuperscript{31} Applying the apparent viscosity model cannot incorporate the key physical mechanisms in nanopores and may overestimate the influence of nanoconfined effects. It is therefore necessary to develop an oil transport model in shale nanopores considering the aforementioned multiple key factors.

Mattia et al.\textsuperscript{40,41} proposed a mathematical formula relating slip length to pore radius, pore length, and surface/liquid molecular interactions based on experiments and MD simulation. Coupling molecular interaction with pore dimension, wall roughness, and temperature, Li et al.\textsuperscript{19} proposed an improved slip length model for nanoconfined water flow. While both models showed good agreement with experimental data for nanoconfined water, they are not applicable in characterizing oil transport behaviors, especially when the microscopic structure of the liquid molecule is taken into consideration. This may be attributed to the fact that the strong interactions between the first layer molecules and the pore surface were ignored, and this made it impossible to incorporate the effects of adhesion of molecular structure. Sun et al.\textsuperscript{1} introduced a correction factor to extend Mattia’s model to a wider range of liquids, which bridged water and oil flows. However, the calculation of the physical quantity of the correction factor was not given, and it is still an empirical value obtained by experiments. Wu et al.\textsuperscript{8} proposed a slip length model, which depends on liquid molecular mobility as well as the ratio of relaxation time between the bulk and the interfacial region without considering pore surface roughness. All these models neglected the adsorption phenomenon of some components of the liquid on the nanotube wall. Due to the complex molecule structure of crude oil, neglecting the adsorption phenomenon can lead to deviations from the real conditions.\textsuperscript{1,20,22} It has also been documented that the components absorbed on the wall surface can be regarded as rock matrix due to the irreversibility of the adsorption process. Based on Mattia’s model, Cui\textsuperscript{20} established a mathematical model incorporating the effects of the originally mixed wettability and the mechanisms triggered by organic matter. However, the applicability of the model to liquids with different molecular structures is still in doubt. In addition, the adsorption of organic matter in oil shale can lead to wettability alteration and other mechanisms. Nevertheless, there are few researches that quantified the impacts of mixed wettability, adsorbed organic matter, pore surface roughness, and liquid molecule structures in shale oil reservoirs.

In this paper, an improved analytical model, with a wide range of adaptability, incorporating the effects of mixed wettability, molecular structure, mechanisms triggered by organic matter, heterogeneous viscosity, and pore surface roughness, is established. With in-depth theoretical investigation, the flow mechanism of oil in mixed wettability nanopores is revealed. Comprehensive sensitivity analysis and comparisons with simplified models are conducted to illustrate oil transport behaviors in shale rocks. Meanwhile, the effects of different adsorption patterns and surface roughness are discussed in detail.

### 2. MODEL DESCRIPTION

The unique flow behavior of confined oil can be investigated in terms of interfacial and viscous resistances.\textsuperscript{8} The interfacial interaction (liquid–wall), intermolecular interaction, and the physical connection (liquid–liquid) are further responsible for interfacial resistance and viscous resistance. These dominate the transport mechanisms of confined oil, similar to water flow in nanopores. The interfacial resistance can be described by the slip length.\textsuperscript{17} Blake\textsuperscript{42} proposed a model based on molecular-kinetic theory to quantitatively calculate the slip length between a liquid and a solid. Wu et al.\textsuperscript{8} extended the scope of application of Blake’s model to the transport of n-alkanes on different solid surfaces. It is noted that the specific value of molecular mobility for different nanopore surfaces is given by Wu et al.\textsuperscript{8} Their expression for slip length is as follows:

\begin{equation}
l_s = \frac{\delta}{\frac{T}{T_\infty}} e^{-\frac{W}{kT}} - 1 \end{equation}

In eq 1, \(\tau\) is the natural relaxation time and subscripts \(\infty\) and \(b\) represent the first-layer molecules for the nanoconfined fluid and the bulk fluid molecules, respectively. \(\delta\) is the average distance between the adjacent layer oil molecules. Note that \(\delta\) in eq 1 is 0.5 nm, \(T\) is temperature, and \(k\) is the Boltzmann constant. \(W\) is the difference in activation energy for the fluid molecule displacement between the nanoconfined fluid and the bulk fluid, which can be expressed as:\textsuperscript{42}

\begin{equation}W = \beta S \sigma (1 - \cos \theta)\end{equation}

where \(S\) is the equivalent wall area of a hole into which a neighboring molecule can move, \(\beta\) is the proportion of the equivalent wall area made up by a solid wall, \(\sigma\) is the surface tension of oil in a vacuum, and \(\theta\) is the contact angle of the oil on the solid surface in a vacuum. For n-alkanes with different chain lengths, \(\beta S\) is obtained as:\textsuperscript{43,44}

\begin{equation}\beta S = \frac{\pi}{6} [0.1265(n - 1) + 0.46] \end{equation}

The correlation between the contact angle and the interfacial tensions is Young’s equation:\textsuperscript{45}

\begin{equation}\cos \theta = -1 + 2\varphi \sqrt{\frac{\sigma}{\sigma_i}}\end{equation}

where \(\sigma\) is the surface energy of nanopore wall in a vacuum and the coefficient \(\varphi = 0.85\), which is a function of the surface tension.\textsuperscript{45} Combining eqs 1–4 yields the slip length for oil molecules with different chain lengths:

\begin{equation}l_s = \delta \left(\frac{\delta}{\frac{T}{T_\infty}} e^{-\frac{W}{kT} \left[0.1265(n - 1) + 0.46\right] (1 - \cos \theta)} - 1\right)\end{equation}

where \(n\) is the carbon number of the oil molecule.
In this section, an equivalent boundary slip length model based on eq 5 incorporating mixed wettability, pore surface roughness, and effect of adsorbed organic matter is established. In addition, an improved flow enhancement model is also established. As shown in Figure 1, complex conditions of wettability and organic matter adsorption is observed in a real shale nanopore. These lead to changes in average flow resistance, which influences the behavior of oil molecules transport. The adsorbed organic matter can reduce the radius of flow conduit and change the initial mixed wettability of the pore surface.

2.1. Effect of Mixed Wettability. The shale nanopores are composed of organic and inorganic surfaces (Figure 1), which should be considered and incorporated into the mixed wettability model in shale. The equivalent activation energy for the fluid molecule can be obtained by the arithmetic average:

\[ W_{\text{eff}} = \alpha W_i + (1 - \alpha) W_o = \alpha \beta \sigma_{\alpha \beta} (1 - \cos \theta_i) + (1 - \alpha) \beta \sigma_{\alpha \beta} (1 - \cos \theta_o) \]  

(6)

where \( \alpha \) is the area ratio of the water-wet surface and subscripts \( i \) and \( o \) stand for organic and inorganic surfaces, respectively. Unlike the treatment of the activation energy, the equivalent relaxation time can be calculated by the theory proposed by:

\[ \tau_{\text{eff,UB}} = \frac{N_i}{N_i \sum_{j=1}^{N_j} \frac{1}{\sum_{i=1}^{N_i} k_{ij}}} = \frac{1}{\tau_i + \frac{1 - \alpha}{\tau}} \]  

(10)

\[ \tau_{\text{eff,UB}} = \frac{N_i}{N_i \sum_{j=1}^{N_j} \frac{1}{\sum_{i=1}^{N_i} \tau_{ij}}} = \alpha \tau_i + (1 - \alpha) \tau_o \]  

(11)

\[ \tau_{\text{eff}} = \sqrt{\tau_{\text{eff,LB}} \tau_{\text{eff,UB}}} = \left( \frac{1}{\frac{\alpha \tau_i + (1 - \alpha) \tau_o}{\tau}} \right)^{\frac{1}{2}} \]  

(12)

where \( \tau_{\text{eff}} \) is the statistical average of relaxation time and \( \tau_{ij} \) is the relaxation time of the grid \((i, j)\).

2.2. Effect of Pore Surface Roughness. Note that the slip length depends on the contact angle, which is related to the oil–wall molecular interactions (eq 5), which has obvious impacts on the slip length. The greater the interactions (or the greater the nanopore wall surface energy), the smaller the contact angle. However, surface roughness plays a significant role in the value of the contact angle. When the contact angle is in the range of 0° to 90°, the contact angle becomes smaller due to the wall roughness. Besides, considering the low surface tension of the oil molecule compared to the nanopore wall, the oil can spread out to a contact angle lower than 90° on the wall. Wenzel defined the apparent contact angle \( \theta_{\text{app}} \) on a rough surface as:

\[ \cos \theta_{\text{app}} = r_A \cos \theta \]  

(13)

where \( \theta_{\text{app}} \) is the apparent contact angle and \( r_A \) is a surface roughness factor that is equal to the ratio of the actual area to a projected area. On a rough surface, the features of rough elements are usually irregular and self-affine, which can be described by fractal theory as:

\[ r_A = \left( \frac{l}{l} \right)^{D-2} \]  

(14)
where \( l_i \) and \( l_f \) are upper and lower boundaries of rough elements, \( D \) is the roughness fractal dimension.

### 2.3. Effect of Organic Matter Adsorption

The wettability and pore radius of a flow conduit can be influenced by adsorption of organic matter. Due to the complex adsorption phenomenon, two parameters, namely, surface coverage ratio and adsorption thickness, are taken into consideration in discussing the effect of adsorbed organic matter. In fact, deposition of the organic matter comes along with its adsorption, which leads to slight changes in oil physical properties. These factors are not discussed in this work for simplicity.

#### 2.3.1. Wettability Alteration

The initial area of the inorganic surface occupied by the organic matter can be determined by the surface coverage ratio and the original inorganic surface ratios. The property of the organic matter is assumed to be the same as the original organic surface. When the adsorbed organic matter is randomly distributed, the inorganic surface ratio can be determined as follows:

\[
\alpha_i = \alpha(1 - \gamma)
\]

\[
\alpha_r = 1 - \alpha_i = 1 - \alpha(1 - \gamma)
\]

where \( \alpha_r \) is the inorganic surface ratio, \( \alpha_i \) is the organic surface ratio, \( \gamma \) is the surface coverage ratio of the organic matter.

#### 2.3.2. Pore Radius Reduction

Assuming that the mobility of the adsorbed organic matter is very low, the pore radius of the flow conduit will decrease and this phenomenon is represented mathematically as:

\[
r = r_0(1 - \gamma h_i)
\]

where \( r_0 \) is the originally nanopore radius and \( h_i \) is the thickness of adsorbed organic matter.

### 2.4. Equivalent Boundary Slip Length and Flow Enhancement Model

Although the nanoconfined oil flow obeys continuum hydrodynamics, the traditional no-slip Hagen–Poiseuille relation fails to characterize the liquid transport behavior in nanopores due to the strong interactions caused by nanoconfined effects. Introducing the effects of all the aforementioned conditions discussed in Sections 2.1 to 2.3, the equivalent slip length can be expressed as:

\[
l_s = \delta(\tau c W_{ef} - 1)
\]

where \( W_{ef} \) and \( r \) are constants, which are utilized to simplify the complexity of the results. The exact expressions for \( W_{ef} \) and \( r \) are given below:

\[
W_{ef,i} = \alpha(1 - \gamma)\beta \delta \eta_i \left[ 1 - \left( \frac{l_f}{l_i} \right)^{D-2} \cos \theta_i \right] + [1 - \alpha(1 - \gamma)]\beta \delta \eta_i \left[ 1 - \left( \frac{l_r}{l_i} \right)^{D-2} \cos \theta_r \right]
\]

\[
\tau_r = \frac{\tau_0}{\sqrt{\frac{\alpha(1 - \gamma) + [1 - \alpha(1 - \gamma)]\eta_i}{\eta + \frac{\alpha(1 - \gamma) + [1 - \alpha(1 - \gamma)]\eta_i}{\eta}}}}
\]

Nanoconfined liquids exhibit complex behaviors compared to its bulk region, including enhanced viscosity of the interfacial region and prolonged relaxation time (as illustrated in Figure 1). Although it is difficult to measure the viscosity of the interfacial region, the viscosity of a nanoconfined liquid correlates well with its location time:

\[
\frac{\eta_{inf}}{\eta_b} = \frac{\tau_0}{\tau_b}
\]

where \( \eta \) is the liquid viscosity, \( \tau_0 \) is the average relaxation time of the fluid located in the interfacial region. In addition, the heterogenous distribution of physical properties leads to the appearance of velocity distribution in the interfacial and bulk regions. Similar to the treatment of equivalent relaxation time, the equivalent viscosity can be obtained as:

\[
\eta_{ef} = \sqrt{\frac{\alpha(1 - \gamma)\eta + [1 - \alpha(1 - \gamma)]\eta_b}{\frac{\alpha(1 - \gamma)}{\eta} + \frac{1 - \alpha(1 - \gamma)}{\eta_b}}}
\]

The two velocity models have been widely applied to explore the transport behavior of nanoconfined liquids. The bulk and near-wall velocities have the following expressions, respectively:

\[
v_b = \frac{1}{4\eta_{inf}}(r_0^2 - r^2) + \frac{1}{4\eta_{inf}}(r_0^2 - r_b^2) + \frac{r_0}{2\eta_{inf}}l \frac{\Delta p}{l}, r \in [0, r_b]
\]

\[
v_{io} = \frac{1}{4\eta_{inf}}(r_0^2 - r_{io}^2) + \frac{r_0}{2\eta_{inf}}l \frac{\Delta p}{l}, r \in [r_{io}, r_0]
\]

where \( \Delta p \) is the externally applied pressure gradient with pore length of \( l \) and \( v \) is the velocity. \( r_b \) is the thickness of bulk region \( r_b = r_0 - h_i \) and \( h_i \) is the thickness of the interfacial region. According to previous studies of nanoconfined oil flow, the thickness \( h_i \) was reasonably assumed to be 0.96 nm, representing an approximately two-molecular layer thickness. Integrating eqs 23 and 24 over the radius of the circular nanopore in each section gives:

\[
q_b = \frac{\pi}{8\eta_{inf}} \left[ r_0^4 + 2\eta_{inf} (r_0^2 - r_{io}^2) + 4\eta_{inf} r_0^2 r_{io} \right] \frac{\Delta p}{l}
\]

\[
q_{io} = \frac{\pi}{8\eta_{inf}} \left( (r_0^2 - r_{io}^2) (r_0^2 - r_{io}^2 + 4r_0 l) \right) \frac{\Delta p}{l}
\]

where \( q \) is the liquid flux. The total volumetric flux of liquid transport in the circular nanopore can then be expressed as:

\[
q = q_b + q_{io} = \frac{\pi}{8\eta_{inf}} \left[ r_0^4 + \eta_{inf} (r_0^4 - r_{io}^4 + 4r_0^3 l) \right] \frac{\Delta p}{l}
\]

Note that in cases where \( l_i = 0 \) and \( h_i = 0 \), eq 27 can be reduced to the no-slip Hagen–Poiseuille equation:

\[
q_{np} = \frac{\pi r_0^4 \Delta p}{8\eta_{inf} l}
\]

The flow enhancement is defined as the ratio of actual volumetric flux to the no-slip Poiseuille flux with the following expression:
Based on the discussions above, the full expression for the flow enhancement is obtained as:

\[
\varepsilon = \left( 1 - \eta_r \right) + \frac{\eta_0}{\eta_{\infty}} \left( 1 + \frac{4\delta}{r_0 - \gamma h_0} \right)
\]

(29)

where \( \eta_r \) is a constant, which is utilized to simplify the complexity of the results. The exact expression for \( \eta_r \) is given as:

\[
\eta_r = \frac{\eta_0}{\sqrt{\frac{\alpha(1-\gamma)\eta_1 + (1 - \alpha)(1-\gamma)\eta_1}{\alpha(1-\gamma) + (1-\alpha)(1-\gamma)}}}
\]

(31)

The aforementioned mechanisms have complex influences on oil transport behavior. The surface coverage can lead to changes in wettability, pore radius of flow conduit, and viscosity of the interfacial region. To investigate the contributions of these critical factors, several simplified expressions of eq 30 are derived for comparisons and analysis:

1. Ignoring wettability alteration \((\gamma = 0)\):

\[
\varepsilon = \left( 1 - \eta_r \right) + \frac{\eta_0}{\eta_{\infty}} \left( 1 + \frac{4\delta}{r_0} \right)
\]

(32)

2. Ignoring reductions in the pore radius \((h_a=0)\):

\[
\varepsilon = \left( 1 - \frac{h}{r_0} \right) + \eta_1 \left[ 1 + 4\delta \left( \tau e^{w_{av}} - 1 \right) \right]
\]

(33)

3. Ignoring spatial distribution of viscosity \((\eta_r=1)\):

\[
\varepsilon = \left[ 1 + \frac{4\delta}{r_0 - \gamma h_0} \right] \left( \tau e^{w_{av}} - 1 \right)
\]

(34)

3. MODEL VALIDATION

In order to validate the proposed model presented in this study, the results of previous experiments/simulations studies are adopted. Notably, the inorganic surface ratio and other variables (surface coverage, adsorption thickness, and roughness fractal dimension) are difficult to determine. Thus, the proposed model is validated by the simplified formula:

Table 1. Summary of Parameters Used in the Validations

| researcher     | alkane | \( \sigma_s, \mu N/m \) | \( \sigma_l, \mu N/m \) | \( \sigma_0, \mu N/m \) | \( 2r_0, \text{nm} \) | \( T, \text{K} \) | \( \tau_{\infty}/\tau_b \) |
|----------------|--------|------------------------|------------------------|------------------------|------------------|----------------|---------------------|
| Karan et al.53,54 | C_{6}  | 26–27                  | 18.4                   | 1.4                    | 293.15           | 1.31–1.34      |
| Yang et al.56   | C_{6}  | 78.9                   | 18.4                   | 1                      | 293.15           | 6.50           |
| Wang and Fichthorn56 | C_{10} | 1000                   | 48.3                   | 1.01                   | 2685             | 2685           |
| Xia et al.57    | C_{16} | 1270                   | 45.94                  | 1–4.0                  | 76.85            | 1,000,000      |
| Chandramoorthy and Hadjiconstantinou58 | C_{16} | 2400                   | 29.45                  | 1.1–10.5               | 176.85           | 270            |
| Karger et al.59 | C_{6}-C_{14} | 500            | 45.77–30.44            | 0.5–0.75               | 24.85            | 60–40,000      |

"Surface tension data was from the National Institute of Standards and Technology (NIST)."
were strongly a considered and it was assumed that the contact angles for the proposed model, the structure of oil molecules (n-alkanes) inorganic pores and other parameters are listed in Table 2. Moreover, in deriving the predicted results from eq 35 are shown in Figure 2.

The parameters used in the validations are listed in Table 1. The predicted results from eq 35 are shown in Figure 2. It is observed from Figure 2 that the proposed model had good agreement with previous studies. This showed that the proposed model revealed the transport behavior of oil in nanopores for different oil molecules with varying size and surface energy at varying temperatures.

4. RESULTS AND DISCUSSIONS

The primary parameters used in the proposed mixed wettability model are listed in Table 2. Previous studies reported distinct transport behavior in organic and inorganic pores and attributed this observation to the significant differences in pore wettability and pore sizes. Organic pore sizes are usually smaller than inorganic pores and most of their surface areas are covered by organic matter. This can be attributed to oil–wall interactions that are dominated by the surface energies of the nanopore wall. Meanwhile, the surface energy of inorganic pores is larger than that of organic pores.

In this study, therefore, the pore size \( r_0 \) and the initial inorganic surface ratio were determined as: \( r_{0,i} = 5 \) nm, \( \alpha = 0.2 \) for organic pores and \( r_{0,o} = 20 \) nm, \( \alpha = 0.8 \) for inorganic pores. The other parameters are listed in Table 2. Moreover, in deriving the proposed model, the structure of oil molecules (n-alkanes) was considered and it was assumed that the contact angles were strongly affected by the surface tension of the oil molecules. The surface tensions of n-alkanes with different carbon numbers and relaxation time ratio for organic and inorganic pores are shown in Figure 3. It is worth mentioning that the relaxation time can be obtained by molecular dynamic simulations and experiments, including Rayleigh-wing scattering, Raman spectroscopy, nuclear magnetic resonance, time-resolved phosphorescence, and optical Kerr effect spectroscopy. The values of the relaxation time ratio in Figure 3 were taken from Wu et al.\textsuperscript{8}

It could be seen from eq 29 that the chain length of n-alkanes, pore radius, initial inorganic surface ratio, surface coverage, adsorption thickness, and wall roughness were directly related to the stated mechanism. In this study, other variables were regarded as constant values. All of these factors are discussed in this section, and the contributions of mechanisms mentioned in section 2 are explored as well.

4.1. Effect of Chain Length of n-Alkanes

From Figures 4 and 5, it was noted that chain length had a significant effect on flow behavior of n-alkanes, which were confined in nanopores. Flow enhancement increased with the increase in the carbon number. It was also observed that flow enhancement spanned over three and two orders for organic and inorganic pores, respectively, but decreased to as low as 10–1 for \( C_6 \) confined in a nanopore. This phenomenon is confirmed by experiments of pulsed-field gradient NMR spectroscopy. \textsuperscript{61,62} Although the mobility of longer chain length oil molecules was smaller, the flow enhancement was greater. A possible explanation for the high flow enhancement factors is that the longer chain molecules became more entangled with neighboring layer-molecules. This rendered the longer chain molecules near the pore surface to be easily affected by the corresponding bulk molecules. Therefore, cohesion of long chain n-alkanes would be stronger than their adhesion to the wall. In addition, the flow enhancement of organic pores was more sensitive (increased rapidly) to the chain length but less sensitive for inorganic pores. This can be attributed to the larger slip length of organic pores compared to that of inorganic pores.

As shown in Figures 4 and 5, the contributions of each mechanism changed with the increment in chain length of

![Figure 3](https://dx.doi.org/10.1021/acsomega.0c04678)  
Figure 3. Surface tension and relaxation time ratio versus carbon number of alkanes at a pressure of 0.101 MPa and temperature of 293.15 K.
organic and inorganic pores. The two factors that contributed most were wettability alteration and spatially varying viscosity. As the chain length increased, the contributions of wettability alteration and spatially varying viscosity increased and this indicated that the nanoscale effects reflected by wettability alteration and spatially varying viscosity should not be neglected in inorganic nanopores. However, the influence of pore radius reduction was negligible when the carbon number was larger than 10. As the flow enhancement factors for C_{16} had the longest span (over three orders), subsequent calculations and analysis were based on that of C_{16}.

### 4.2. Effect of Pore Radius

Pore radius, which is in the range of 0-500 nm, plays an important role in oil flow behavior at the nanoscale. The other parameters used for the calculations can be found in Table 2. The effect of pore radius and the contributions of each stated mechanisms are shown in Figures 6 and 7.

It is observed from Figures 6 and 7 that flow enhancement factors increased rapidly with decreasing pore radius, with values between 3 and 400 for organic pores and 0.75 and 7.5 for inorganic pores. This showed that the flow capacity of oil in certain situations would decrease. When the pore radius was large enough, the influence of boundary slip became gradually smaller. However, the pore radius had different influences on contributions of wettability alteration for organic and inorganic pores. When the wettability alteration was ignored, the slip length was less than 0. Therefore, the flow enhancement factor for inorganic pores increased with the increase in pore radius. Meanwhile, the flow enhancement factor for inorganic pores was less than 1 when the wettability alteration was ignored. This observation can be attributed to the negative slip length and the high viscosity of the interfacial region. When the viscosity was high enough, the interfacial region liquid was difficult to mobilize and could be regarded as a reduced pore size. For organic pores, pore radius reduction was negligible and the impacts of wettability alteration and viscosity increment were dominant. Meanwhile, for inorganic pores, due to the smaller pore radius of flow conduit and the lower slip length, the pore radius reduction led to a decrease in flow enhancement.
In some previous studies, the critical pore radius that the slip phenomenon is negligible is approximately 10 nm. However, the critical pore radius of this research was far greater than 10 nm and varied with pore types (larger than 500 nm for organic pores and about 250 nm for inorganic pores). This can be explained by the different liquid–wall interactions for different chain length oil molecules. This means the molecular structure should be considered in nanoconfined flow.

4.3. Effect of Initial Inorganic Surface Ratio. Figures 8 and 9 show the relationship between the flow enhancement factor and the initial inorganic surface ratio considering different mechanisms. The initial wettability condition played an important role in oil flow behaviors in organic and inorganic nanopores. The flow enhancement factor rapidly decreased with the increase in the initial inorganic surface ratio. In fact, the increasing initial inorganic surface ratio meant higher equivalent viscosity and smaller slip length at the nanoscale. More inorganic surface offered higher chances for wettability alteration. For organic pores, a smaller initial inorganic surface ratio was favorable for its flow enhancement, while for inorganic pores, a moderate initial inorganic surface ratio was most beneficial for its flow enhancement factor. Meanwhile, the existence of adsorbed organic matter enhanced the oil flow capacities for both organic and inorganic pores.

4.4. Effect of Surface Coverage. From Figures 10 and 11 it was noted that the surface coverage had positive influences on the flow enhancement for organic pores. Meanwhile, until the contribution of the surface coverage was high enough for inorganic pores, its influence on flow enhancement was not obvious. The increment of surface coverage meant that the organic pore surface ratio further increased. This led to an increment in the equivalent slip length and a decrement in the equivalent viscosity. Thus, the mobility of oil molecules became higher. Comparison between Figures 10 and 11 showed that the influences of surface coverage for organic pores were more sensitive than it was for inorganic pores. The difference can be explained by the distinct initial inorganic surface ratio for organic and inorganic pores. The equivalent slip length for organic pores was high. However, for inorganic
pores, the equivalent slip length was a negative value when the surface coverage was small and the influences of increasing the surface coverage gradually became obvious. Compared to wettability alteration and viscosity increment, the effect of pore radius reduction was negligible. Meanwhile, the difference between the influence of pore radius reduction of organic and inorganic pores was well noted. From Figures 10 and 11, it was observed that reduction in pore radius improved flow enhancement for organic pores. Meanwhile for inorganic pores, reduction in pore radius decreased flow enhancement initially but increased it subsequently. This meant the equivalent slip length for inorganic pores was initially smaller than 0 nm but was subsequently greater than 0 nm. Obviously, the adsorbed organic matter and the spatially varying viscosity played important roles in oil transport behaviors at the nanoscale.

4.5. Effect of Relative Adsorption Thickness. As illustrated in Figures 12 and 13, the adsorption thickness had less influence on the flow enhancement of organic and inorganic pores. The flow enhancement of inorganic pores had a slight increase with high adsorption thickness. Meanwhile, the change in flow enhancement of inorganic pores was not easily noticeable. For both organic and inorganic pores, the pore radius reduction had no initial impact on the enhancement factor but, subsequently, the enhancement factor increased. Furthermore, the impact of spatially varying viscosity on enhancement factor almost never changed. Meanwhile, the impact of wettability alteration for inorganic pores was higher than that for organic pores. This could be explained by the negative equivalent slip length for inorganic pores. The adsorption region reduced the flow conduit pore radius, and this further increased the impact of negative slip flow. Moreover, the viscosity of the interfacial oil region in inorganic pores was much higher than that of organic pores. In summary, the existence of adsorbed organic matter would enhance the flow capacity of organic pores but reduce that of inorganic pores. The contribution of adsorbed organic matter was not sensitive to the relative adsorption thickness.

4.6. Effect of Pore Surface Roughness. In this section, the relationship between flow enhancement factor and
Figure 10. Effect of surface coverage for organic pores.

Figure 11. Effect of surface coverage for inorganic pores.

Figure 12. Effect of relative adsorption thickness for organic pores.
Figure 13. Effect of relative adsorption thickness for inorganic pores.

Figure 14. Effect of roughness fractal dimension for organic pores.

Figure 15. Effect of roughness fractal dimension for inorganic pores.
roughness fractal dimension is discussed. The contributions of each mechanism were explored as well, as shown in Figures 14 and 15. The ratio of the upper to lower boundaries ($\frac{\alpha}{\beta}$) was set as 3. From Figures 14 and 15, it was observed that the flow enhancement factor initially decreased and then tends to be a constant value with an increasing roughness fractal dimension. The reason was that the surface energy of the nanopore wall was much lower compared to the surface tension of oil molecules. This led to a contact angle, which was generally smaller than $90^\circ$, and the apparent contact angle approached $0^\circ$ due to the increasing wall roughness. The pore radius reduction initially increased the flow capacity but subsequently reduced it in organic pores. For inorganic pores, however, the pore radius reduction decreased the flow enhancement factor. This meant that the equivalent slip length decreased with an increasing surface roughness fractal dimension. When the wettability alteration was ignored, the oil flow in inorganic pores was insensitive to the surface roughness because of the lower intrinsic slip length. This indicated that the effect of adsorbed organic matter depended on nanopore types.

5. CONCLUSIONS

An analytical model for shale oil transport capacity is proposed in this paper considering multiple key mechanisms including the effects of mixed wettability, adsorbed organic matter, and spatially varying physical properties. Notably, the equivalent slip length and equivalent viscosity within the interfacial region were related to oil−wall interactions and oil molecule structures. For adsorbed organic matter, the effects of wettability alteration and pore radius reduction were incorporated into the model. The main conclusions of the present work are as follows:

(1) The proposed model revealed oil flow behavior in mixed wet shale nanopores. The new model is more universal in practice as it considered oil molecules with different chain lengths and multiple mechanisms triggered by adsorbed organic matter.

(2) The flow enhancement factor was sensitive to the pore radius, initial inorganic surface ratio, surface coverage, and pore surface roughness for both organic and inorganic pores. Meanwhile, adsorption thickness had almost no influence on oil transport behavior. The flow enhancement of organic pores was more sensitive than that of inorganic nanopores.

(3) Generally, the adsorbed organic matter enhanced the oil flow capacity in organic pores but reduced it in inorganic pores. This was due to the different slip lengths and the distinct pore radius scales of organic and inorganic pores.

(4) The wettability alteration and the viscosity increment of oil within the interfacial region were the dominant influencing factors of oil transport behavior in shale nanopores. High oil viscosity in the interfacial region played a negative role and led to a significant reduction in the flow enhancement factor. However, wettability alteration played a positive role and resulted in a significant increase in the flow enhancement factor. The effect of pore radius reduction was negligible for organic pores. For inorganic pores with higher surface roughness and larger pore radius, however, there was a significant error in the estimation of the overall flux if reduction in pore radius was neglected.

■ AUTHOR INFORMATION

Corresponding Author
Guoxiang Zhao — College of Petroleum Engineering, China University of Petroleum, Beijing 102249, China; orcid.org/0000-0002-0984-8513; Email: gary9221@163.com

Authors
Yuedong Yao — College of Petroleum Engineering, China University of Petroleum, Beijing 102249, China
Caspar Daniel Adenutsi — Core and Rock Properties Laboratory, Department of Petroleum Engineering, Faculty of Civil and Geo-Engineering, Kwame Nkrumah University of Science and Technology, Kumasi AK, Ghana
Xiaolong Feng — No.1 Oil Production Plant, Changqing Oilfield, PetroChina, Yan’an 716000, China
Lian Wang — College of Petroleum Engineering, China University of Petroleum, Beijing 102249, China
Wenwei Wu — Ningbo Fengcheng Advanced Energy Materials Research Institute, Ningbo 315000, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04678

Notes
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■ NOMENCLATURE

$l_i$ (nm) slip length
$\delta_i$ (nm) average distance between the adjacent layer oil molecules
$\tau_{i\alpha}$ (s) natural relaxation time for the first-layer molecules
$\tau_{\omega\alpha}$ (s) natural relaxation time for the bulk fluid molecules
$W$ (J) difference in activation energy for the fluid molecule displacement between the nanoconfined fluid and the bulk fluid
$k_B$ (J/K) Boltzmann constant
$T$ (K) temperature
$\beta$ proportion of the equivalent wall area constituted of a solid wall
$S$ (nm$^2$) equivalent wall area of a hole into which a neighboring molecule can move
$\sigma$ (mN/m) surface tension of oil in a vacuum
$\sigma_e$ (mN/m) surface energy of nanopore wall in a vacuum
$\theta$ (°) contact angle
$n$ carbon number of n-alkanes
$\alpha$ area ratio of the inorganic surface
$k_w$ statistical average
$N_{\alpha}$ number of grids in columns
$N_{\beta}$ number of grids in rows
$k_{\alpha\beta}$ permeability of the grid $(i, j)$
$\tau_{i\omega\alpha}$ (s) statistical average of relaxation time
$\tau_{\omega\alpha}$ (s) relaxation time of the grid $(i, j)$
$\theta_{eq}$ (°) apparent contact angle
$\alpha_{eq}$ surface roughness factor
$l_u$ upper boundaries of rough elements
$l_l$ lower boundaries of rough elements
D roughness fractal dimension

γ surface coverage ratio of organic matter

η_{eq}(mPa s) equivalent viscosity

v_{l}(nm/s) bulk and near-wall velocities

v_{w}(nm/s) near-wall velocities

l(nm) pore length

ΔP(MPa) externally applied pressure difference

r_{0}(nm) pore radius

r_{j}(nm) thickness of bulk region

h_{j}(nm) thickness of interfacing region

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