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Full Length Article

Inherent wettability of different rock surfaces at nanoscale: a theoretical study

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ABSTRACT

Investigating the inherent wettability of rock surfaces at nanoscale is of great importance in ore floatation and oil recovery field. Using molecular dynamics simulations, we systematically study the wetting behavior of water on different rock surfaces (silica, calcite, gypsum, halite and graphite) at nanoscale. It is demonstrated that the inherent rock wettability follows the order of gypsum > calcite > halite > silica > graphite. Remarkably, we also manifest that the polarity of oil molecules can affect the water contact angles on silica surface. For example, the water contact angles on silica surface in hexane, dodecane, thiophene and toluene are $58 \pm 2^\circ$, $63 \pm 3^\circ$, $90 \pm 1^\circ$, $118 \pm 1^\circ$, respectively. Furthermore, we investigate the wetting behavior of water on heterogeneous rock surfaces and find that water molecules can move from hydrophobic surface to hydrophilic surface.

1. Introduction

With increasing demand of crude oil, efficient oil recovery is becoming more and more crucial. Until now, various oil recovery technologies have been widely used to enhance oil recovery [1–5]. Relevant research has shown that oil detachment efficiency can be significantly affected by inherent rock wettability, which is determined by complex interface boundary condition [6]. In addition, the inherent rock wettability has a direct effect on multiphase flow, such as oil and water transport in the nanopores of shale rocks. Subsequently, investigations of the rock wettability have attracted some attention, which contributes to solving oil shortage problems. Moreover, understanding the wetting behavior of water on rock surface can also shed light on various technological and scientific fields, such as self-cleaning textile [7], antifogging glass [8], antifouling marine coatings [9], biomimetic materials [10], water purification [11], stable emulations [12] and oil-water separation [13,14].

The wettability is usually evaluated by contact angle θ, which is formed between the oil-water interface and water-solid interface, as shown in Fig. 1. Based on the Young's equation [15], θ can be defined using the following equation:

$$\gamma_{so} = \gamma_{sw} + \gamma_{ow} \cos\theta \quad (1)$$

where γ_{so} is the interfacial tension between rock surface and oil, γ_{sw} is the interfacial tension between rock surface and water, γ_{ow} is the interfacial tension between oil and water, respectively. It should be noted that the rock surface is considered hydrophobic if θ is higher than 90° or hydrophilic if θ is lower than 90°. In recent years, some experiments have been conducted to measure contact angles in rock systems [16–18]. Using axisymmetric drop shape analysis, Yang et al. [19] found that oil recovery was significantly affected by wettability alteration. They also found that the equilibrium contact angles between oil and rock reservoir increased with increasing pressure, whereas it decreased with increasing temperature. By the pendant-drop shape analysis, Ameri et al. [20] investigated contact angles in two kinds of rock system and they found that in water-wet rock system, the contact angle decreased with increasing brine salinity while the contact angle was a constant with increasing pressure. However, for oil-wet rock system, the contact angle increased linearly from 95° to 150° between 4 MPa and 10 MPa while the contact angle remained a constant with increasing brine salinity. Using captive bubble method, Seyyedi et al. [21] found that carbonated water injection could improve waterflood

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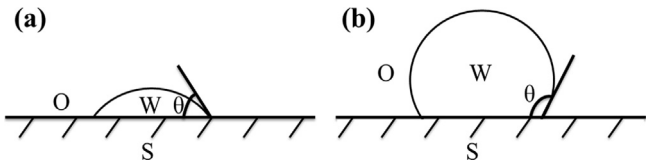

Fig. 1. Contact angle θ resulting from the balance of interfacial tensions, (a) hydrophilic surface, (b) hydrophobic surface. (S, O, W represent solid, oil, water, respectively).

performance and further alter the wetting characteristics of the surface. For example, they observed that the contact angle decreased from 89° to 63° for the aged mica surface and from 144° to 97° for the aged calcite surfaces due to the injection of carbonated water.

Notably, wettability can be significantly affected by surface contamination and roughness [22–25]. It is shown that the wettability of solid surface is easily affected by the adsorbed contamination [22] and that the roughness [24,25] of solid surface has an effect on the spreading of water droplet on solid surface, which contributes to the difficulty of experimentally obtaining inherent rock wettability. Importantly, previous works have shown that the inherent wettability of surface at nanoscale plays a decisive role in oil transportation in nano-sized channel [26,27]. Hence, it is valuable to find a feasible method to study inherent rock wettability at nanoscale, which can provide guidance in shale oil recovery.

Recently, molecular dynamics (MD) simulations have been developed to investigate inherent contact angles on solid surface at nanoscale, such as water on graphene [28–30], water on various metals [31–34], water on Na-montmorillonite surfaces [35], aqueous nanodrops on chemically heterogeneous surfaces [36], water droplets on nanopillared hydrophobic surfaces [37]. Using MD simulations, Wang et al. [38] found that appropriate charge quantity and distribution could lead to an interesting phenomenon of "water that does not wet a water monolayer" on a solid surface at room temperature. Combining MD simulations and quantum chemical calculations, Guo et al. [39] revealed that water molecules could be embedded in carboxyl-terminated self-assembled monolayers due to hydrogen bonding network. Taherian et al. [40] theoretically found that the water contact angle on graphite was 90° while the water contact angle on graphene was 127°. Besides, they found that the contact angle could be affected by the interaction potential energy between water and graphene. Halverson et al. [41] calculated the contact angle of surfactant solutions on hydrocarbon surfaces with the support of MD simulations using all-atom force fields. They found that trisiloxane surfactants could promote the complete wetting of aqueous droplets on hydrophobic materials. Zhong et al. [42] investigated the conformational change of the oil droplet on different self-assembled monolayer surfaces in aqueous solution via MD simulations. They found that rock wettability had great effect on the conformation of oil droplet on the mineral surfaces.

The above literature survey indicates that investigations about the effect of oil phases and heterogeneous rock surfaces on the wetting behavior of water on different rock surfaces and the corresponding mechanisms are still deficient. In this paper, we will systematically study the inherent rock wettability at nanoscale, which is the basis of understanding wettability of rock surface in shale oil recovery. Firstly, MD simulations are employed to investigate the wetting behavior of water on different rock surfaces (silica, calcite, gypsum, halite and graphite) in dodecane phase. Then, the interaction energy between dodecane molecules and rock surface as well as the interaction energy between water molecules and rock surface is calculated to explain the wetting mechanism of different rock surfaces. Besides, the water contact angles on silica surface in different oil phases are calculated. Lastly, the wetting behavior of water on heterogeneous rock surfaces in hexane phase is studied.

2. Models and methods

2.1. Models

The initial rock models are derived from the structural database of Material Studio (MS) software. Repeat units of silica, calcite, gypsum, halite and graphite are cleaved along the (100) crystallographic orientation. Among these rock surfaces, silica surface is modified with hydroxyls groups to ensure the structural stability [43], which is a common silica surface in oil recovery. Besides, all the rock surfaces are cleaved with the thickness of 9.5 Å, as shown in Fig. 2. Hexane, dodecane, thiophene, toluene and pyridine molecules are selected as different kinds of oil molecules, respectively, as shown in Fig. 3. Meanwhile, oil-water box (310 dodecane and 1000 water molecules) is shown in Fig. 4a. The initial simulation models used in our work consist of oil, water and rock surface, as shown in Fig. 4b. The size of oil-water-rock box is about $70 \times 50 \times 50$ Å^3.

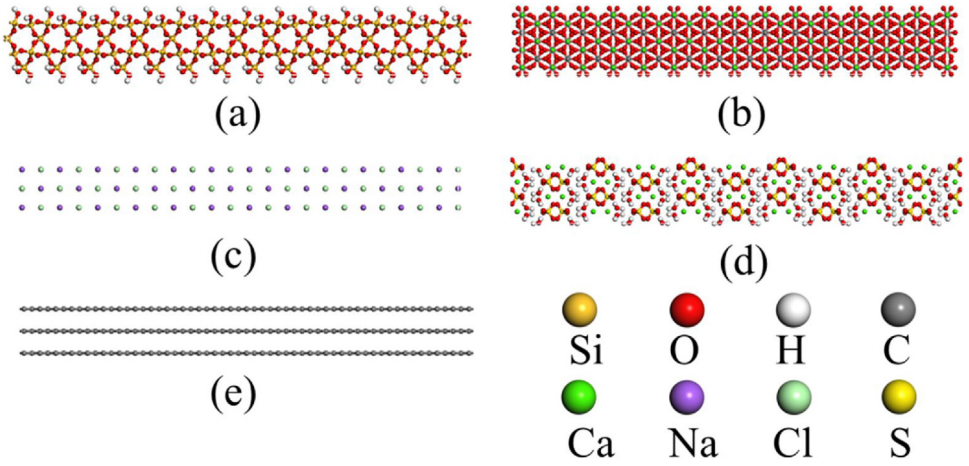

Fig. 2. Rock surfaces used in this work, (a) silica surface, (b) calcite surface, (c) halite surface, (d) gypsum surface, (e) graphite surface. (Golden, red, white, gray, green, purple, aqua, yellow balls represent silicon, oxygen, hydrogen, carbon, calcium, sodium, chlorine, sulphur atoms, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)