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Pore Wetting Phenomena: Implications to Enhanced Oil Recovery and Geologic Carbon Storage

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Abstract

Pore wetting has been considered as an important factor in carbon storage and enhanced oil recovery. Previous studies were limited to the wetting measurements on flat substrates; few measurements were directly carried in a pore to indicate the pore wetting. In this paper, we used the pore contact angle measurement technique recently developed in our laboratory to measure the contact angles of fluids in a single capillary, by considering the effects of pore size, applied pressure and temperature and three different CO₂ phases (gas, liquid and supercritical). The results indicate that the pore wetting only significantly changes on the CO₂ phase transition boundary and then remains unchanged. The effects of pressure and temperature are not significant on the pore wetting when there is no CO₂ phase variation. Our data conclude that the pore wetting of liquid in presence of CO₂ is in the order of $\theta_{\text{gas CO}_2} < \theta_{\text{supercritical CO}_2} < \theta_{\text{liquid CO}_2}$. The pore wetting varies with glass pore size and applied liquid. The contact angles measured in a glass pore are significantly different from the ones measured on a flat glass substrate.

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Keywords: Pore wetting, supercritical CO₂, Contact angle, CO₂ storage, Enhanced oil recovery

1. Introduction

The safe CO₂ geological storage has become one of the most promising technologies to control the greenhouse gas emission. If the depleted oil reservoir is considered for CO₂ storage, it has the additional benefit that CO₂ injected into the reservoir will enhance the recovery of oil, thus making the CO₂ storage more economically feasible. The efficiency and safety of this process depend on the fluid-fluid and rock-fluid interactions inside the porous media. For example, the final storage capacity and total amount of capillary-trapped CO₂ of the porous reservoir are affected by the interfacial tension between the fluids and the contact angle between the fluids and the rock mineral surface. The interfacial tensions of reservoir

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fluids under various reservoir conditions have been widely and well investigated. However, the wetting of mineral surface in the presence of CO₂ and reservoir fluids becomes controversial in recent studies. [1, 2] It is therefore necessary to work on this further. To date, studies on wetting have been limited to observations on flat substrates; few studies were carried in pores. Pore wetting is an important factor governing the displacement of two immiscible phases in porous materials. Due to lack of a technique for measuring the contact angle in a small pore, the pore wetting is often simply estimated by the contact angle measured on a flat surface, which might be relevant in some cases but deserves to be assessed. Thus, we used an experimental rig recently developed in our laboratory [3, 4] to directly measure the contact angles of fluids in a small pore. The pore contact angles obtained from the experiments will significantly enhance the understanding of pore wetting in carbonate aquifers, and oil and gas reservoirs.

2. Materials and Methods

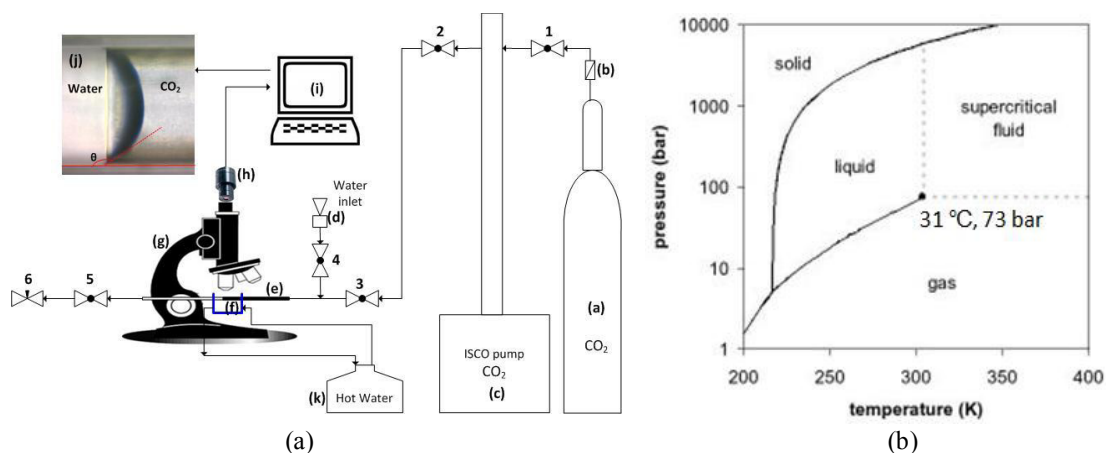


Fig. 1. (a) Experimental setup: (a) CO₂ cylinder, (b) CO₂ filter, (c) ISCO CO₂ pump, (d) water injector, (e) capillary tube, (f) hot water bath chamber, (g) optical microscope (Olympus, BHW) with a 10X objective, (h) digital camera (AM7023, Dino-Eye), (i) data acquisition computer, (j) CO₂-water pore contact angle image; 1-5: ball valve, 6: needle valve; (b) CO₂ phase diagram

The experimental rig in Fig 1 (a) was designed to measure CO₂-liquid contact angles in a single capillary under extreme conditions such as those encountered in geological CO₂ storage, like high pressure and temperature. The fluids used include CO₂, distilled water and n-decane. The pore used is a FEP (Fluorinated ethylene propylene) capillary whose diameter is 250 μm. The setup can handle the pressure up to 100 bar. A hot water bath was used to elevate the temperature of CO₂/water or CO₂/decane interface. Two temperatures were involved in this study, which are 20 °C (ambient temperature) and 40 °C. The whole system is first flushed with CO₂ to remove air. Then, close valve 3 and inject water or decane into the capillary by (d) to make sure that the capillary is full of water/decane, and then close valve 6. When the operating pressure is set by the constant-pressure mode of the ISCO CO₂ pump, valve 3 is opened to slightly release the needle valve 6 to let CO₂ displace water/decane in the capillary at a constant pressure. When the CO₂/liquid interface entered the measurement zone under the microscopy, the valve 5 was quickly switched off. There will be no flow in the system and the pump stops pumping. When any dynamic movement of CO₂/liquid interface is completely stopped, equilibrium CO₂-liquid contact angle can be achieved and then analyzed. In this study, we also used this technique to measure the pore contact angles of DI water, 1-propanol, n-decane and crude oil in glass capillaries with a size range from 100 to 1000 μm at ambient conditions.

3. Results and Discussion

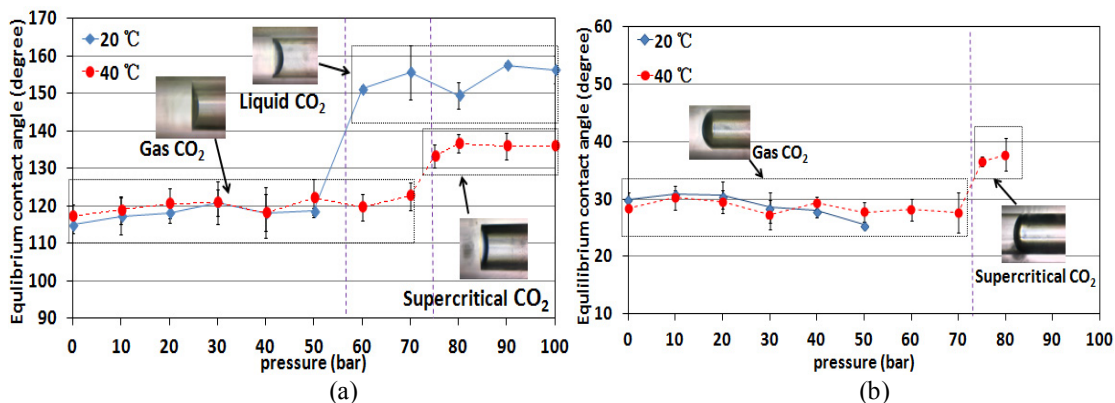


Fig. 2. (a) CO₂-water contact angles and (b) CO₂-decane contact angles at various pressures from 0 to 100 bar and 20 °C and 40 °C

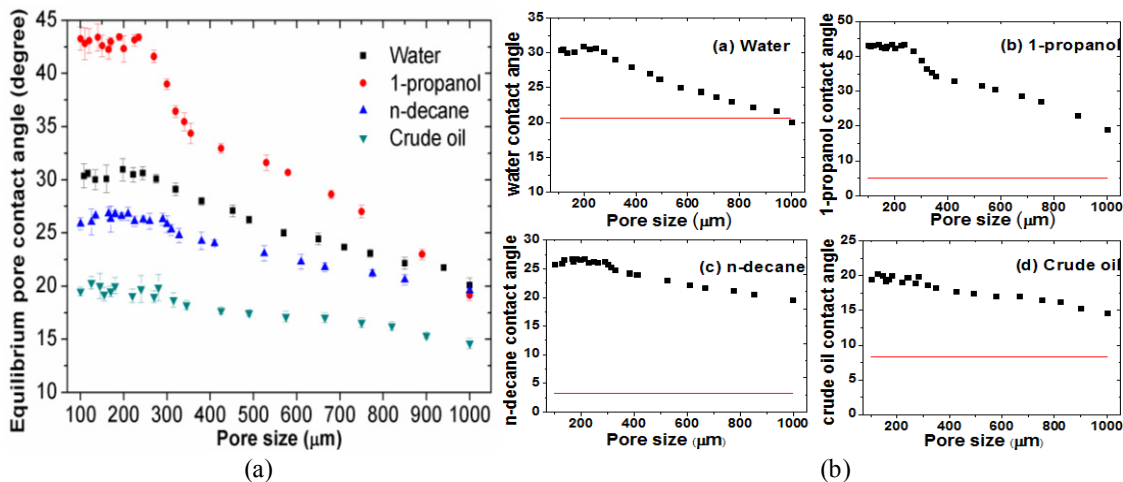


Fig. 3. (a) Pore contact angles of water, 1-propanol, decane and crude oil in glass capillaries with a size range from 100 to 1000 μm; (b) Comparison of pore contact angles with contact angles on a flat surface. ■ Pore contact angle; ● Contact angle on a flat surface.

Fig.2 shows the equilibrium CO₂-water and CO₂-decane contact angles in a FEP pore at various pressures ranging from 0 to 100 bar and at two different temperatures (20 °C and 40 °C). The phase of CO₂ varies with the applied pressure and temperature, as shown in Fig.1 (b). At ambient temperature (20 °C) CO₂ turns from gas phase to liquid phase at approximately 60 bar. If both temperature and pressure increase to be at or above the critical point (31 °C and 73 bar), CO₂ would be at supercritical state. In this study, we investigated the effects of pressure, temperature and CO₂ in three different phases (gas, liquid and supercritical) on the CO₂-liquid contact angle in a capillary. When the applied temperature is 20 °C, CO₂ cannot reach the supercritical state, so only gas and liquid of CO₂ are involved in the contact angle trend for 20 °C. Fig.2 (a) indicates that the gas CO₂-water pore contact angle remains almost constant around 115° at the pressure range from 0 to 50 bar. When the pressure increases over the CO₂ liquid-vapour boundary pressure of 60 bar, the contact angle suddenly increases to approximately 150°. The contact angle of liquid CO₂-water does not vary with the pressure increase. At the operating temperature of 40 °C, CO₂ changes from gas phase to

supercritical phase when the applied pressure increases over the critical pressure of around 73 bar. The contact angle trend at this elevated temperature indicates that the surface become less water-wet in presence of supercritical CO₂ than gas CO₂. The wettability change only occurs on the phase transition boundary and then remains unchanged. The gas CO₂-water contact angle at 40 °C keeps around 118° which is very close to the ones at 20 °C. So, the effect of temperature on the gas CO₂-water contact angle is not significant in this study. When the pressure increases over 73 bar, the CO₂-water contact angle suddenly raises from 118° to 135°. The supercritical CO₂-water contact angle remains at around 135°, which does not vary with the operating pressure. Similarly, Fig.2 (b) shows the CO₂-decane pore contact angles under various pressures and temperatures. At 20 °C, the gas CO₂-decane pore contact angles keep around 28° at a pressure range from 0 to 50 bar. The gas CO₂ dissolves in decane at around 52 bar at 20 °C. At 40°C, the CO₂-decane pore contact angle significantly increases from 28° to 38° when the CO₂ turns from gas to supercritical phase at 73 bar. So, it can be concluded that the CO₂-liquid pore wetting can be only altered significantly when the CO₂ phase changes. It does not obviously vary with applied pressure and temperature if there is no phase change. The pore wetting of water in presence of CO₂ is in the order of $\theta_{\text{gasCO}_2} < \theta_{\text{supercritical CO}_2} < \theta_{\text{liquid CO}_2}$.

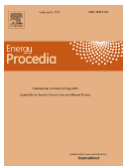
Fig.3 (a) shows that contact angle of a liquid in a glass pore increases with pore size decrease. When pore size of glass capillary decreases from 1000 to about 300 μm, water contact angle increases from 20° to 30°, 1-propanol contact angle increases from 19° to 39°, n-decane contact angle increases from 20° to 26° and crude oil contact angle increases from 15° to 20°. There is no significant inconsistency regarding the dependence of contact angle on glass pore size with a size range from 100 to 300 μm. These results are compared with their contact angles on a flat substrate in Fig.3 (b). Contact angles in glass pores largely differ from the contact angles measured on flat glass surfaces. The pore contact angle tends to draw close to its contact angle on a flat surface when the pore size is big enough. Since these contact angles were measured directly in a pore, these data can be directly applied into capillary resistance calculation in order to contribute to determine CO₂ injectivity, the sealing capacity of geological formation and oil recovery efficiency during carbon storage and enhanced oil recovery processes.

Acknowledgements

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Biography

Xingxun Li received BEng degree in Chemical Engineering in the University of Edinburgh in 2010 and obtained Msc in Advanced Chemical Engineering in Imperial College London in 2011. At present, he is doing PhD. in multiphase flow transport and wettability under the supervision of Dr. Xianfeng Fan in School of Engineering, University of Edinburgh, UK.