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WETTABILITY CHANGE TO GAS-WETNESS IN POROUS MEDIA

Kewen Li and Abbas Firoozabadi

Reservoir Engineering Research Institute (RERI)

Abstract

In the petroleum literature, gas is assumed to be the non-wetting phase and liquid the wetting phase. For gas-liquid systems in porous media, it is often assumed that $q = 0^{o}$, and $\cos q = 1$. While the contact angle for the gas-liquid systems may be small, it may not be zero as is often assumed. In fact, simple measurements in a capillary tube show that the contact angle for gas-liquid systems may be greater than zero. It could be as large as 50^{o}. However, to the best of our knowledge, there is no published work that the wettability of the porous media can be made gas-wet. There are a number of applications where gas-wet porous media will help to improve the efficiency of the recovery process. One such application is the improvement of gas well deliverability in gas condensate reservoirs. This is the main motivation for our efforts to alter the wettability of porous media from liquid-wet to gas-wet. We use two different groups of chemicals for wettability alteration.

Prior to wettability alteration, the capillary rise in the tube and the imbibition of water and normal-decane in the air-saturated Berea are measured. The same measurements after wettability alteration are repeated. Results show that in the capillary tube the contact angle after wettability alteration by one chemical changes to $q = 90^{o}$, and 60^{o} for water-air and normal decane-air systems, respectively. In Berea sandstone, instead of some 60 percent imbibition, there is no imbibition with water and a substantial reduction in the imbibition of normal decane. Another chemical has a more pronounced effect on the wettability alteration to gas-wetness. For the glass capillary tube, the contact angle changes to $q = 120^{o}$ and 60^{o}, for water-air and normal decane-air systems, respectively. For Berea sandstone, neither water nor normal-decane imbibes in the air-saturated Berea after wettability alteration. The above simple tests and a number of other tests give a clear demonstration that the wettability of porous media can be permanently altered to gas-wetness.

Introduction

Certain gas condensate reservoirs experience a sharp drop in gas well deliverability when the reservoir pressure drops below the dewpoint [1-3]. Examples include many rich gas condensate reservoirs that have a permeability of less than 100 md. In these reservoirs, it seems that the viscous forces alone cannot enhance gas well deliverability. One may suggest liquid removal around the wellbore by phase behavior effects through CO_2 and propane injection. Apparently both have been tried in the field with limited success; the effect of fluid injection around the wellbore for the removal of the condensate is temporary.

Wettability can be a very important parameter for the enhancement of gas well deliverability. If one can alter the wettability of the wellbore region to intermediate gas-wetness, gas may flow efficiently in porous media.

The effect of wettability in hydrocarbon production is widely acknowledged. As early as 1941, Buckley and Leverett [4] recognized the importance of wettability on water flooding performance. Later, many authors have studied the effect of wettability on capillary pressure, relative permeability, initial water saturation, residual oil saturation, oil recovery by water flooding, electrical properties of reservoir rocks, and reserves [5-10, 12-15]. In 1959, Wagner and Leach [6] reported the possibility to improve oil displacement efficiency by wettability adjustment during water flooding. In 1967, Froning and Leach [7] reported a field test in Clearfork and Gallup reservoirs for improving oil recovery by wettability alteration. Kamath [8] made a review of wettability detergent flooding. He noted that it was difficult to draw a definite conclusion regarding the success of detergent floods from the data available in the literature. Penny et al. [11] reported a technique to improve stimulation by wettability alteration for gas-water-rock systems. A surfactant was added into the fracturing fluid. The production following cleanup after fracturing in gas wells generally was 2 to 3 times greater than field averages or offset wells treated with conventional techniques. Penny et al. [11] believed that the increased production was due to wettability alteration. However, there was no demonstration that the wettability has been altered.

Most of these studies described above were done in oil-water-rock systems instead of gas-liquid-rock systems (gas-oil or gas-water-rock systems). In the petroleum literature, gas is assumed to be the non-wetting phase and liquid the wetting phase. For gas-liquid systems in porous media, it is often assumed that the contact angle, $\theta = 0^o$, and $\cos\theta = 1$ (contact angle is measured through the liquid phase). While the contact angle for gas-liquid systems may be small, it may not be zero as is often assumed in the literature. When a small amount of liquid is put inside a capillary tube and it is held in the vertical position, the liquid may not flow. Analysis of this simple experiment using the following equation

$$h_l = \frac{2\sigma}{\Delta\rho g r}(\cos\theta_R - \cos\theta_A)\,, \qquad (1)$$

reveals that the contact angle is not zero. Eq.1 is derived from the force balance between the gravity and capillary forces. The symbols are: h_l the liquid height held in a circular capillary tube of radius r, θ_R the receding contact angle and θ_A the advancing contact angle, $\Delta\rho$ the density difference between the gas and liquid phase, and σ the surface tension. There are also indications that in porous media the contact angle may not be zero in gas-liquid systems; it is of the order of several degrees or more but not intermediate gas-wet. It is also often assumed in the petroleum literature that the contact angle in gas-liquid system will not be changed substantially.

As mentioned before, some gas condensate reservoirs experience a sharp drop in gas well deliverability when the reservoir pressure drops below the dewpoint [1-3]. There may be two methods to enhance gas well deliverability in gas condensate reservoirs. In one approach, the gas-liquid surface tension can be reduced (provided it is not too low) by using a chemical such as a surfactant. There are two drawbacks for this approach: 1) there is a need for continuous or batch injection of the surface tension lowering agent, and 2) the surface tension may not be significantly reduced to a low enough value to enhance the gas relative permeability. The first and second shortcomings are serious enough for many practical applications. In the second approach, one may alter the wettability around the wellbore to gas-wetness permanently. If this can be done, gas well deliverability enhancement will be significant. The main challenge is how to alter the wettability of porous media to gas wetness. We have developed a technique to change the wettability of glass capillary tubes, Berea and other rocks very efficiently from strong liquid-wetness to gas-wetness both in the gas-oil and gas-water systems by using chemicals with low concentrations. The wettability in porous media is evaluated by spontaneous imbibition and entry capillary pressure measurements. In the following, we will present the results of our work.

Theory

To the best of our knowledge, wettability alteration to gas-wetness has not been suggested in the petroleum literature. Consider the sketches provided in Fig.1. In Fig.1a, when the contact angle, q, < 90^o, the liquid will rise in the circular capillary tube inserted vertically in the liquid. If $q = 90^o$, there will not be liquid rise (see Fig.1b). When $q > 90^o$, the liquid level will go down in the circular capillary tube as sketched in Fig.1c. The rise and fall of the liquid are given by

$$h_l = \frac{2s\ cosq}{Drgr} . \qquad (2)$$

Eq. 2 can be used to estimate q, once h_l, s, $\Delta\rho$, and r are known.

Experimental

In the experimental work, brine, water and normal-decane were used as the liquid, air as the gas phase, and glass capillary tube, or Berea as the substrate. Two types of chemicals were employed to alter the wettability of a substrate. The experiments were conducted at a room temperature of 20^oC.

Fluids Normal-decane was used as the oil phase; its specific gravity and viscosity are 0.73, 0.95 cp at 20^oC, respectively. The surface tension of the air-normal-decane system is 23.4 dynes/cm at 20^oC. Brine of 1.0 percent NaCl was used as the water phase in Berea experiments; its specific gravity and viscosity are 1.01 and 1.0 cp at 20^oC. The distilled water was used as the water phase for the experiments in the capillary tube; the surface tension of air-distilled water system is 72.1 dynes/cm at 20^oC.

Core and Capillary Tube In order to study the alteration of wettability to gas-wetness, we used two different substrates: 1) capillary tube, and 2) rock. The glass capillary tube used in our work has an internal diameter of 0.23 mm. The Berea sample has a permeability of about 500 md and a porosity of 21.8 percent. The diameter and the length of Berea are 5.02 cm and 5.06 cm, respectively (PV = 21.82 ml).

Chemicals Two groups of chemicals were used to alter the wettability in the experiments. We call these Chemicals A and B. Chemical A is inexpensive and Chemical B is more expensive. Chemical A is a cationic surfactant and is water-soluble. The specific gravity (at 25°C) and the flash point of Chemical A are 1.15 and 23°C, respectively. Chemical B is a polymer with molecular weight of about 100,000 and it is neither soluble in water nor in oil. Chemical B can be dissolved in a fluorocarbon-type solvent. It is mixed with a fluorocarbon diluent for the chemical treatment of the substrate; the specific gravity of the diluent is around 1.7 at 25°C.

Procedure The chemicals described above are prepared and the glass capillary tube and Berea are aged in them for a certain period of time. Then the capillary tube and Berea are evacuated and dried to remove the liquid chemicals. A very small amount remains on the substrate as an adsorbed layer, which decreases the surface energy and renders the solid surface gas-wet.

Both chemicals A and B were used to alter the wettability of glass capillary tube and Berea sandstone. Prior to wettability alteration, the capillary rise of liquid (oil or water) in the tube and the imbibition of water and oil in the air-saturated Berea were measured in both gas-oil and gas-water systems, respectively. The same measurements were repeated after wettability alteration.

Results

We have conducted a number of tests in the capillary tube and rock. The experimental results are discussed in the following.

Capillary Tube Tests

Chemical A Fig. 2 shows liquid rise vs. the concentration of Chemical A (in the treatment process) for both the gas-oil and gas-water systems; the liquid rise in the capillary tube decreases with an increase of the concentration and then stays constant when the concentration reaches 0.2%(wt). The reduction of the water rise due to wettability alteration is much more pronounced than that of the oil. The contact angle can be calculated using Eq. 2. Fig. 3 plots the computed contact angle vs. the concentration of Chemical A for the gas-oil and gas-water systems. Note that the contact angle prior to treatment is about 50 ° for gas-water system and about 0 ° for a normal decane-air system. This figure shows that the contact angle increases with the increase of the concentration; the contact angle of the gas-water systems increases to about 90 ° at a concentration of 0.1 percent. The implication is that wettability of the gas-water-glass system has been altered to intermediate gas-wetness by Chemical A. The contact angle of gas-oil increases to about 60 ° at a concentration of 0.1 percent; the wettability alteration in the gas-water system by Chemical A is more pronounced than that in the gas-oil system.

Chemical B Fig. 4 shows the liquid level vs. the concentration of Chemical B for both the gas-oil and gas-water systems; liquid level in the capillary tube decreases with an increase of the concentration. The effect of the chemical concentration on the liquid level is reduced when the concentration is higher than about 0.1 percent. The interesting observation in this figure is the fall of the water level to negative values in the capillary tube, which confirms the wettability alteration instead of the decrease of the surface tension. It is definitely determined from Eq. 2 that the liquid height in a capillary tube shown in Fig.1 cannot be negative by reducing the surface tension. The only way to have a fall of the liquid level is to alter wettability from liquid-wetness ($q < 90^{o}$) to gas-wetness ($q > 90^{o}$). Fig. 5 plots the computed contact angle vs. the concentration of Chemical B for both gas-oil and gas-water systems; the contact angle is calculated by using Eq. 2. This figure shows that the contact angles of both gas-oil and gas-water in the capillary tube increases with the increase of the concentration. The contact angles of gas-water and gas-oil increase to about 118 ^{o} and 60 ^{o} at one percent concentration, respectively. The wettability alteration in the gas-water system by Chemical B is much more pronounced than that in the gas-oil system.

Berea Imbibition Tests

Chemical A Fig. 6 plots water imbibition in Berea vs. time with and without the treatment of Chemical A. The water imbibition is represented by the fraction of the pore volume (PV) of the core. This figure shows that the imbibition of water in Berea treated by Chemical A is much less than that in Berea without the chemical treatment. The imbibition is related to the wettability and decreases from liquid-wetness to gas-wetness. Therefore, Fig.6 demonstrates that wettability of the gas-water-rock (Berea) system has been altered from strong liquid-wetness to intermediate gas-wetness by Chemical A. Fig. 7 depicts the oil imbibition in Berea vs. time with and without the treatment of Chemical A in the gas-oil-rock system. This figure demonstrates that the wettability of the gas-oil-rock (Berea) system has been altered to less liquid-wetness after treated by Chemical A. Similar to the glass tube, the wettability alteration by Chemical A in the gas-water system is more pronounced than that in the gas-oil system.

Chemical B Fig. 8 shows the amount of water imbibed in Berea vs. time with and without the treatment by Chemical B; water does not imbibe into Berea due to wettability alteration. It can be seen from this figure that the wettability in a gas-water-Berea system has been altered from strong water-wetness to gas-wetness by Chemical B. Fig. 9 shows similar results as in Fig. 8 for the gas-oil system, which implies that the wettability of gas-oil-Berea system can be also altered from strong oil-wetness to gas-wetness by Chemical B.

It can be seen from the results shown in Figs. 8 and 9 that Chemical B is more efficient than Chemical A to alter the wettability in gas-liquid-Berea systems. Work in progress shows other important features of wettability alteration. These features are: 1) permanent wettability alteration with Chemical B, 2) effectiveness of Chemical B for various rock types, 3) a threshold capillary pressure when an air-saturated core is contacted with water or normal-decane liquid. A threshold or entry capillary pressure implies that a definite gas-wetness has been established. All these findings will be published later.

Conclusions

1. The wettability of gas-water-rock (Berea) systems can be altered from strong water-wetness to intermediate gas-wetness by Chemical A and can be altered from strong water-wetness to gas-wetness by Chemical B.
2. The wettability of gas-oil-rock systems can be altered from strong oil-wetness to less oil-wetness by Chemical A and can be altered from strong oil-wetness to gas-wetness by Chemical B.

Acknowledgements

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Nomenclature

h_l = height of liquid column
r = radius of a capillary tube
q = contact angle
q_A = advancing contact angle
q_R = receding contact angle
$\Delta\rho$ = density difference between gas and liquid
s = interfacial tension
m = fluid viscosity

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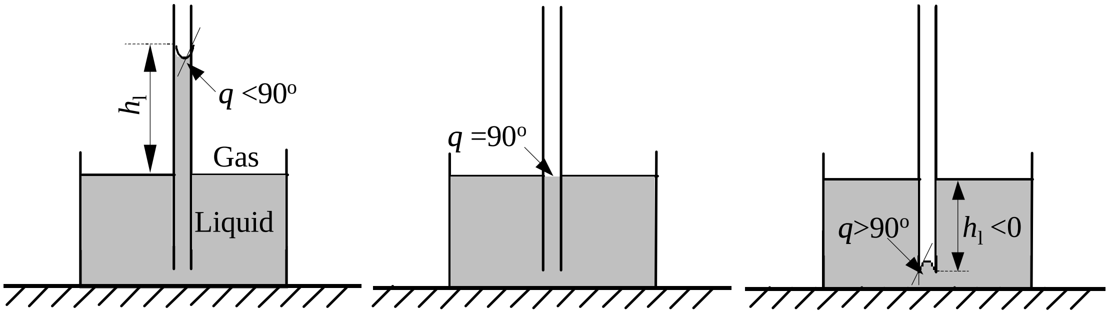

(a) Strong liquid-wet (q <90^o) (b) Intermediate gas-wet (q =90^o) (c) Gas-wet (q >90^o)

Fig.1-Liquid level rise or fall in a capillary tube at various wettability conditions

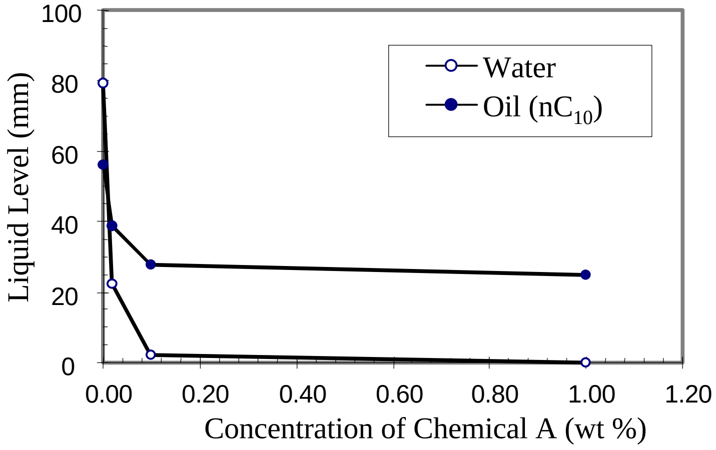

Fig. 2-Liquid level vs. concentration of Chemical A in the glass tube

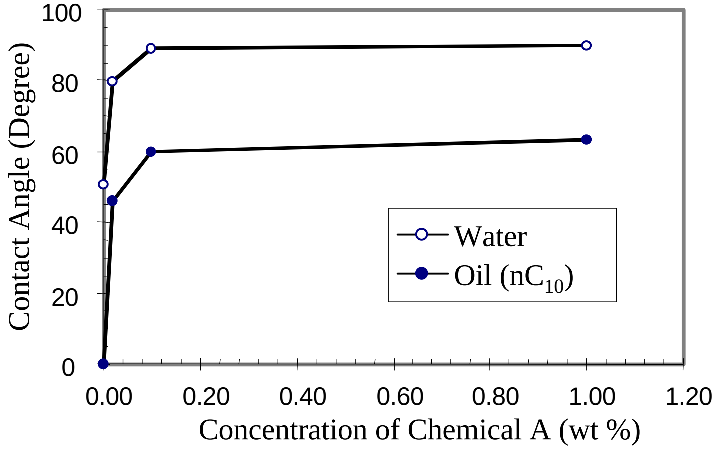

Fig. 3- Contact angle vs. concentration of Chemical A in the glass tube

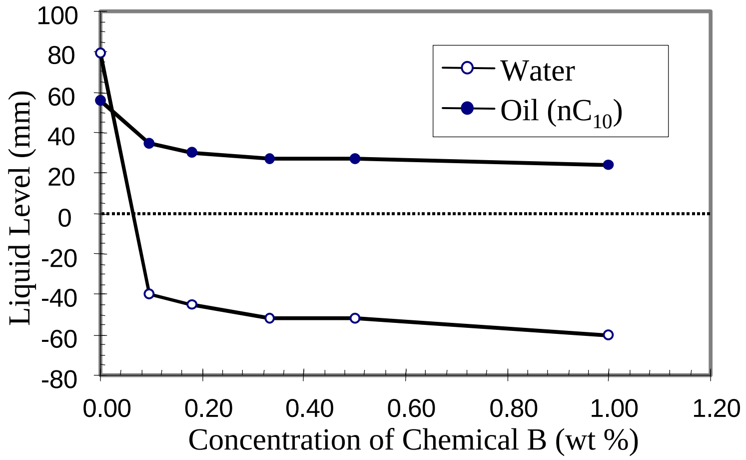

Fig. 4-Liquid level vs. concentration of Chemical B in the glass tube

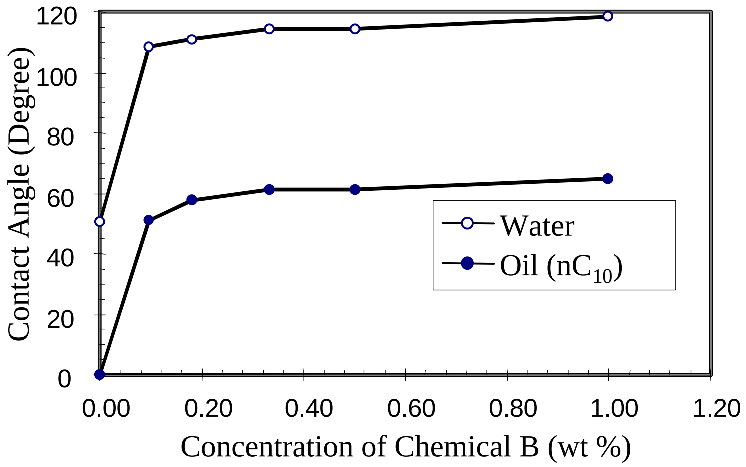

Fig. 5-Contact angle vs. the concentration of Chemical B in the glass tube

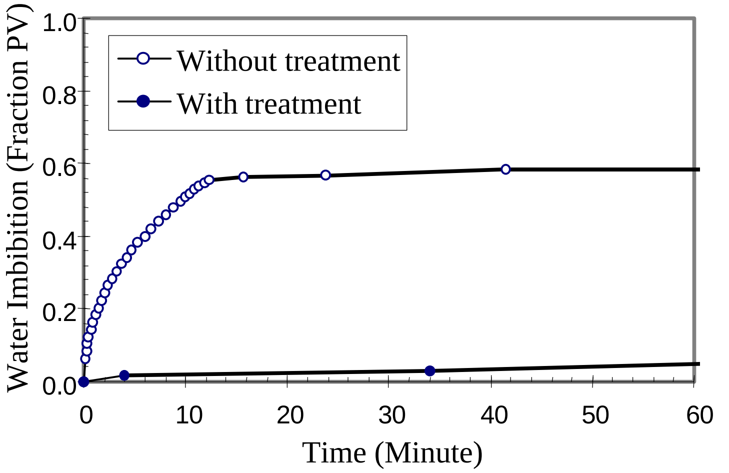

Fig. 6-Water imbibition vs. time with and without the treatment of Berea with 0.1%(wt) Chemical A

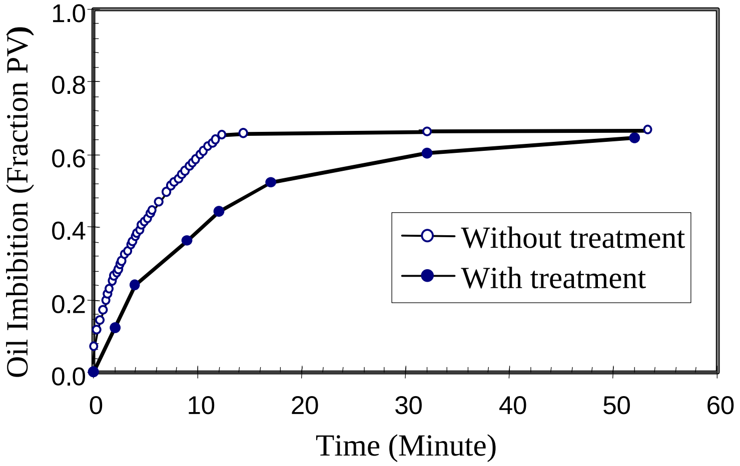

Fig. 7-Oil imbibition vs. time with and without treatment of Berea with 0.1%(wt) Chemical A

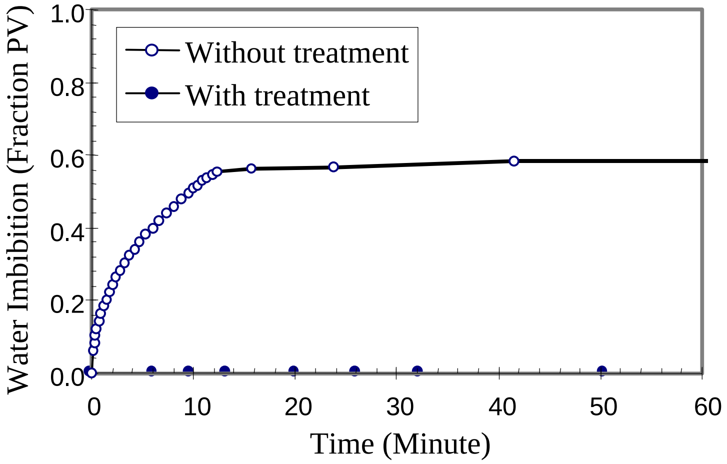

Fig. 8-Water imbibition vs. time with and without treatment of Berea with 0.18%(wt) Chemical B

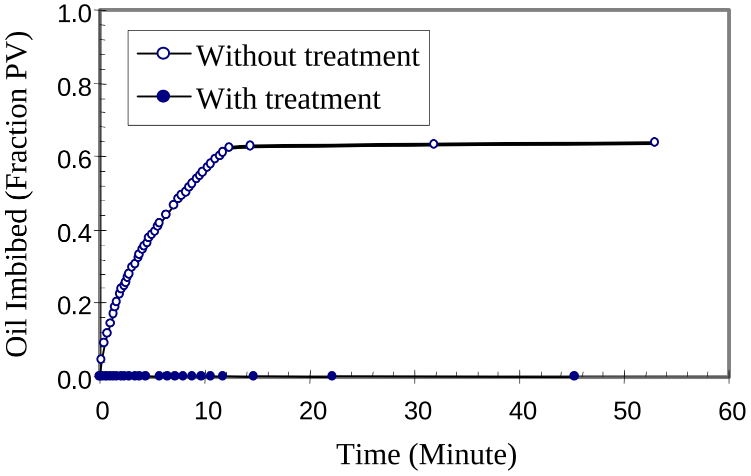

Fig. 9-Oil imbibition vs. time with and without treatment of Berea with 0.18%(wt) Chemical B