Pore-Scale Spontaneous Imbibition at High Advancing Contact Angles in Mixed-Wet Media: Theory and Experiment

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**ABSTRACT:** Mixed wettability develops naturally on a pore scale in oil reservoirs after primary drainage. The invading oil fills pore interiors that become oil-wet by asphaltene deposition, while the residual water retreats into the pore corners, masking them and retaining their water wetness. This wettability alteration hinders oil mobilization during secondary waterflooding. Therefore, a proper understanding of the conditions controlling pore-scale imbibition into mixed-wet pores may lead to a substantial increase in oil recovery from the portions of reservoir rocks bypassed during the original waterflooding. We use selective silane coating to fabricate reservoir-representative mixed-wet capillaries with angular cross-sections. We validate our procedure on silica and glass substrates and characterize the mixed-wet surfaces by atomic force microscopy, scanning electron microscopy, and contact angle measurements. Subsequently, we investigate experimentally the invasion of water against air in mixed-wet, water-wet, and oil-wet square capillaries and compare our findings with the theoretical predictions of dynamic (Washburn, Szekely, and Bosanquet) and quasi-static [Mayer-Stowe-Princen (MSP)] meniscus-invasion models. None of the dynamic models for ducts of uniform wettability can fully describe our experimental data in mixed-wet capillaries. However, the experimental results agree with the predictions of MSP theory. We discuss the similarities and differences between experiment and theory and the reasons for the failure of the dynamic models. To our knowledge, this is the first direct experimental validation of MSP theory under mixed-wet conditions in such a controlled manner. We confirm the possibility of spontaneous piston-type imbibition with high (>90°) advancing contact angles into mixed-wet pores, given that the contact angle is lowered below a critical value that is a function of the pore geometry and water saturation. In oil reservoirs, injection of custom-designed brines would be required to change the contact angle to values below the imbibition threshold.

**1. INTRODUCTION**

Two-phase capillary flow underlies several important engineering and biological processes, for example, oil recovery from subsurface porous rocks; CO₂ storage; water treatment, for example, purification/desalination and removal of non-aqueous phase liquids; drinking water infiltration in soil; fluid transfer in biological systems, for example, water/gas flow, blood-plasma separation, or glucose monitoring; and fluid transport in porous electrodes. The surface wettability state dictates fluid configurations in pore space. For instance, when a small fluid drop is put on a flat surface, different equilibrium cases are possible: complete wetting, partial wetting, complete non-wetting, or partial non-wetting. These cases are described using a contact line and contact angle the drop attains with the surface and the surrounding fluid. Complete wetting is realized when the equilibrium contact angle is 0° and the liquid spreads completely over the surface. All other states represent different degrees of partial wetting.

As it always happens in nature, no surface is atomically smooth or clean, and thus, the contact line often pins at the asperities or wettability gradients, indicating altered or mixed wettability states and resulting in a contact angle hysteresis. On a flat surface, partial wetting originating from roughness or chemical heterogeneity can be described using the approaches of Cassie and/or Baxter. Often, partial wetting is confused with mixed wetting. However, in the context of this work, mixed wettability originates from phenomena that are fundamentally different from partial wetting.

Mixed wettability naturally develops in some pore systems of subsurface oil-bearing reservoir rocks. For example, in oil reservoirs during primary drainage, the invading oil phase drains the brine that initially fills the porous reservoir rock. The capillary pressure increases with decreasing water saturation, yet some brine stays behind in the pore corners.

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and wall asperities, even at high capillary pressure. After a long exposure time, the invading oil coats the contacted surface, where most pore surface turns oil-wet. The coating mechanism is believed to be associated with surface-active molecules in the oil phase (asphaltenes) that migrate to the oil/water interface and subsequently deposit on the rock surface when thin water films on the surface rupture. The discussion of this process is outside the scope of this article.15−19

As a result of the coating with asphaltenic oil, a peculiar mixed wettability condition establishes in most pores. The pore walls are oil-wet, and the pore corners, filled with water, remain water-wet because asphaltenes are insoluble in water and therefore cannot dissolve and transport through thick water layers to contact the corner walls.16,20 In flow of two immiscible fluids, the wettability state of the host permeable rock plays a pivotal role. Figure 1 shows schematically a cylindrical pore of a square cross-section that is initially water-wet and filled with water (a); the pore develops mixed wettability after oil invasion (b), with the interiors of the pore walls covered with a hydrophobic coating. Oil affinity of large portions of the pore walls hinders oil extraction as injected brine during waterflooding is unable to enter these pores, mobilize the oil, and push it out.

Figure 1. Wettability alteration inside a square pore. (a) Schematic of the cross-section of a water-wet square pore, initially fully saturated with water (in blue). (b) After drainage: wettability alteration occurs as oil invades the central part, displacing water that recedes into the corners masking their surface. The surfaces in contact with the oil become more oil-wet through deposition of asphaltenes.

Such a unique wettability configuration has been an important research subject for many scientific groups.16,21−26 Most of the previous studies, however, are theoretical and computational because the reservoir-representative mixed-wet condition is difficult to realize in a controlled laboratory environment. Many modeling studies assume a partial wetting state, ignoring the mixed-wet nature of individual pores.27−31 We argue that the partial wetting state of reservoir pores in such models does not capture true pore-level physics.

In order to experimentally study the effects of wettability alteration on flow in subsurface reservoir rocks, a common practice in the oil and gas industry is to perform core flooding experiments. The core material is innately opaque to light, and therefore, only history data of two-phase flow can be obtained at the core outlet. If saturation profile characteristics are of interest, high-energy visualization methods, such as X-ray, must be used. Alhammadi et al.32 used X-ray computed tomography to image oil-saturated core samples and measure wettability in situ through pore contact angle distributions. Such core-scale studies are laborious and expensive, and their interpretation is often subjective due to fundamentally skewed rock−brine−oil contrast in X-ray studies.

In order to avoid issues associated with core-plug experiments, 2D micromodels with channels/capillaries that may mimic reservoir wettability properties are used.33 However, establishing the mixed wettability in such a geometry becomes a major challenge. Zhao et al.34 used a partial wetting approach and observed interesting changes in flow patterns. The same observation applies to all other previously published capillary coating techniques that produce capillaries coated with micron-scale films. These methods date back to Taylor35 up until the recently published spin coating methods.36 They, too, produce a uniform partial wetting state throughout a capillary tube or a pore. We, therefore, emphasize that only pore-level mixed wettability is relevant to two-phase flow in an oil reservoir.

Another approach is to alter wettability separately in different regions of a micromodel to produce a heterogeneous porous medium. A good example is the work by Lee et al.37 Despite the valuable insights these studies provide, such wettability conditions again misrepresent the reservoir mixed wettability, where oil-wet and water-wet surfaces co-exist within individual pores. This state of wettability is fundamentally different from regional heterogeneity and uniform wettability alteration. To the best of our knowledge, our true mixed-wet experimental model system is the first of its kind. It correctly represents the wettability of an oil reservoir on a pore scale, allowing studying two-phase flow in a controlled manner, validates the predictions of MSP theory (see below), and can potentially be extended to a pore network model.

In this work, we present a novel methodology for fabricating true mixed-wet angular capillaries that have a wettability state mimicking that in the pores of an oil reservoir (water-wet corners and oil-wet walls). We use these mixed-wet capillaries as a model system to experimentally study invasion water. We attempt to describe our experimental data with the existing 1D dynamic models (Washburn, Szekely, and Bosanquet) for uniform wettability distributions (partial wetting) and quasi-static (MSP) models for true mixed-wet wettability distributions. The theory for equilibrium pore-level configuration was developed by Mayer and Stowe38 and later by Princen.39,40 Their approach was further extended by many authors, for example, refs 41−44.

Experimentally, we show that spontaneous water imbibition into square cylindrical capillaries at large contact angles (>90°) is possible. MSP theory correctly predicts the imbibition conditions for such mixed-wet capillaries. However, the invasion dynamics into the mixed-wet pores cannot be completely described using the dynamic models developed for uniformly wet capillaries, even if an equivalent averaged wettability value and an equivalent hydraulic radius are used. We believe that this is the first experimental demonstration of the pore-level invasion mechanism into faithful mixed-wet analogues of oil reservoir pores.

2. THEORY

Extensive theoretical work has been conducted on capillary-driven flow under different wettability conditions. In this section, we present the widely accepted dynamic and quasi-static models for capillary flow. The presented models are then compared with our new capillary-rise experiments in fully water-wet, fully oil-wet, and mixed-wet conditions in the following sections.

2.1. Capillary Pressure. The Young−Laplace equation describes the relationship between capillary pressure $P_c$ and the
curvature of the interface between different phases using the following expression

\[ P_c = P_{nw} - P_w = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  

(1)

where \( P_{nw} \) and \( P_w \) are the pressures of the non-wetting and the wetting phases, respectively, \( R_1 \) and \( R_2 \) are the two principal radii of curvature, and \( \gamma \) is the interfacial tension between the two fluids. For a circular capillary of a uniform cross-section, eq 1 becomes

\[ P_c = 2\gamma \cos(\theta)/r \]  

(2)

where \( \theta \) is the contact angle, measured through the denser phase, and \( r \) is the radius of the round capillary. The corresponding equilibrium rise height can be directly obtained by equating the capillary pressure to the hydrostatic head.

2.2. Dynamic Models of Capillary Flow. In a dynamic model of capillary invasion, the pressure change and the interface location are estimated at each time step using volume conservation and Poiseuille’s law.53 Below, we illustrate some of the well-known models of 1D flow. These models do not capture corner flow in angular capillaries as they are developed for flow in circular ducts. In order to capture the dynamics of corner flow, a numerical solution of the Navier–Stokes equation in 3D space is required. Nevertheless, the 1D models, as simple as they are, give useful insights into the dynamics of invasion.

2.2.1. Lucas–Washburn. The Lucas–Washburn model describes capillary penetration into a porous medium.46 It uses the Hagen–Poiseuille law to describe the relation between average flow velocity and pressure. It is rigorous for a uniform-cross-section capillary tube or a bundle of capillary tubes. It neglects the inertial forces and the entrance region in the liquid velocity field. The relation between average velocity in the capillary and rise height is captured using eq 3, which results in the initial velocity being finite, making it non-physical. The variation of the model in the absence of the gravitational effect is presented in Supporting Information (Figure S1).

\[ \frac{8\mu}{\rho r^2} \frac{dh}{dt} = \frac{2\gamma \cos(\theta)}{\rho r} - gh \left. \frac{dh}{dt} \right|_{t=0} = \infty \]  

(3)

where \( \mu \) and \( \rho \) are the viscosity and the density of the penetrating fluid, respectively.

2.2.2. Bosanquet. The deficiency of the Washburn model is caused by the quasi-steady-state approximation implied in the Hagen–Poiseuille law. Such an approximation is inappropriate when fast changes take place in both \( h \) and \( dh/dt \). Bosanquet extended the Washburn model to take into account the inertial effects.47 Bosanquet specified a finite value for the initial velocity. Numerical solution of eqs 4 and 5 yields rise height.

\[ \frac{k}{\rho r^2} \frac{d^2h}{dt^2} + \left( \frac{dh}{dt} \right)^2 + \frac{8\mu}{\rho r^2} \frac{dh}{dt} = \frac{1}{\rho} \left( \frac{2\gamma \cos(\theta)}{r} - \rho gh \right) \]  

(4)

\[ \left. \frac{dh}{dt} \right|_{t=0} = \left( \frac{2\gamma \cos(\theta)}{\rho r} \right)^{1/2} \]  

(5)

2.2.3. Szekely. Szekely presented a more precise formulation of the capillary penetration phenomenon. He extended the Washburn model further than Bosanquet by coupling the outside and inside hydrodynamics around the capillary inlet.48 The initial velocity in this model is zero, which is physically correct.

\[ \frac{dh}{dt} \bigg|_{t=0} = 0 \]  

(6)

Rise height is then obtained in an implicit form from the expression

\[ \left( h + \frac{7}{6} r \right) \frac{d^2h}{dt^2} + \frac{5}{4} \left( \frac{dh}{dt} \right)^2 + \frac{8\mu_c}{\rho r^2} \frac{dh}{dt} = \frac{1}{\rho} \left( \frac{2\gamma \cos(\theta)}{r} - \rho gh \right) \]  

(7)

2.3. Quasi-Static Models of Capillary Flow in Angular Ducts. In quasi-static models, fluid displacement is approximated as an evolution from one equilibrium state to the next without considering time. The Young–Laplace equation is used to obtain the pressure difference across the interface. Such models give the necessary conditions for when capillary-driven invasion can occur and when it cannot. The method used in this study is based on the MSP formulation.38–40,49 The MSP method is used to calculate the capillary pressure of a meniscus inside pores of different geometries. The method relies on equating the curvature of the menisci at the corners, which are called corner arc menisci (AMs), to the curvature of the invading interface, namely, the main terminal meniscus (MTM). The AMs have one finite principal radius of curvature, \( r_{\text{AM}} \), while the second radius is infinite. The total curvature: \( \kappa = 1/R_1 + 1/R_2 \) simplifies to \( \kappa = 1/r_{\text{AM}} + 1/\infty = 1/r_{\text{AM}} \) see Supporting Information, Figure S2). The MSP method is valid for interfaces of finite size such that the effect of gravity on the shape of the interface is negligible.

2.3.1. MSP Model of Drainage. We follow a generalization\(^{30}\) of Mason and Morrow’s expressions for the threshold capillary pressures in drainage,\(^{51}\) where the non-wetting phase invades a capillary filled with the wetting phase. Details are in Supporting Information, Section S2. The entry capillary pressure is expressed as

\[ P_t = \frac{\gamma}{r_{\text{AM}}} \left( \frac{L_{\text{nw},\text{w}} \cos \theta_r + L_{\text{nw},\text{nw}}}{A_{\text{nw}}} \right) = \frac{P_{\text{eff}}}{A_{\text{eff}}} \]  

(8)

where \( \theta_r \) is the receding contact angle and \( L_{\text{nw},\text{w}} \) is the total length of the non-wetting/wetting contact (area/unit depth) and \( A_{\text{eff}} \) and \( P_{\text{eff}} \) stand for the effective area filled with the non-wetting fluid and the perimeter of the non-wetting fluid interfaces with the wetting fluid and solid, respectively. \( L_{\text{nw},\text{w}} \) is equal to the sum of the lengths of all AMs. Similarly, the length of the non-wetting/solid contact, \( L_{\text{nw},\text{nw}} \) (area/unit depth) is equal to the perimeter of the duct minus the length of the water-filled corner menisci. Using trigonometry, the expressions for \( A_{\text{eff}} \) and \( P_{\text{eff}} \) are obtained and substituted into eq 8. After some rearrangement, an expression for the AM radius, \( r_{\text{AM}} \) is obtained from the solution of a quadratic equation as

\[ r_{\text{AM}} = \frac{4\gamma \cos \theta_r}{D(\theta_r)(-1 \pm \sqrt{1 + D(\theta_r)/(4\cos^2\theta_r)})} \]  

(9)

where \( r \) is the radius of the inscribed circle of the capillary geometry, see Figure S3. The appropriate positive root of eq 9 is chosen so that the \( r_{\text{AM}} \) of a stable AM is smaller than the
radius \( r \). The factor \( D \) here is a function of the receding contact angle (see Supporting Information, eq S12).

2.3.2. MSP Model of Imbibition. At the end of primary drainage, the remaining wetting phase resides in pore corners as the non-wetting fluid fills the centers of the pores, see Figure 1. For spontaneous piston-type imbibition of the wetting phase into such a configuration to occur, the threshold capillary pressure would be different from that during drainage due to contact angle hysteresis (\( \theta_a > \theta_h \))\textsuperscript{31,42}

Due to contact angle hysteresis, the threshold capillary pressure for piston-type imbibition is different from that in drainage.\textsuperscript{50} Therefore, the AMs remain pinned at their positions at the end of the primary drainage. As the capillary pressure decreases, the hinging angle of the pinned AM, \( \theta_d \), increases to approach the angle corresponding to the pore wall advancing angle. The hinging angle (\( \theta_h \)) is the angle the pinned AMs form against the wall after primary drainage (\( \theta_d \leq \theta_h \leq \theta_a \)). This makes imbibition a problem where the location of the three-phase contact line is fixed and \( \theta_h \) is varied, whereas in drainage, \( \theta_d \) is fixed and the location of the three-phase contact line is changed (see Supporting Information, Figure S3). If the advancing contact angle is not too large (\( \theta_d \leq \theta_{a,max} \) defined below), the invading interface meets the AM at a zero contact angle. The common radius of curvature \( r_M \) of the AMs may be calculated in a similar fashion to drainage by equating it to \( A_{eff}/P_{eff} \). The set of equations describing the imbibition process for square ducts is presented in Supporting Information, Section S2.2.

During waterflooding of oil reservoirs, a water MTM can only proceed into a pore if it makes a contact angle equal to \( \theta_d \) with the interior parts of pore walls that were altered because of exposure to oil. The maximum advancing contact angle at which spontaneous piston-type imbibition can occur, \( \theta_{a,max} \), can be defined by the limit \( P_{eff} = 0 \), which corresponds to zero capillary pressure, at which the imbibition ceases to be spontaneous. For a square capillary, \( \theta_{a,max} \) is expressed as in eq 10. For derivation, see Supporting Information, Section S2.3.

\[
\cos \theta_{a,max} \approx \frac{-1}{\sqrt{2}} \frac{P_{c,max}^{ND} - \cos \theta_a + \sin \theta_d}{\gamma}
\]

Here \( P_{c,max}^{ND} \) is the dimensionless maximum capillary pressure at the end of primary drainage, equal to \( P_{c,max} r^2/\gamma \). From the area occupied by the corner menisci, the remaining wetting-phase saturation, \( S_w \), can be calculated for any level of capillary pressure at or above the entry pressure. For a square duct, it is obtained using eq 11.

\[
S_w = r_M^2 \frac{C_1}{A_t} = \left( \frac{1}{P_{c,max}^{ND}} \right)^2 \left( \frac{C_1}{4} \right)
\]

where \( A_t \) is the total cross-sectional area of the capillary and \( C_1 \) is a function of the contact angle (eq S9). Using eqs 10 and 11, the maximum advancing contact angle can be obtained for different values of residual saturation after primary drainage. In the following sections, we use these theoretical developments to interpret our experimental results of capillary invasion into mixed-wet channels with modified surfaces of advancing contact angle larger than 90°.

3. EXPERIMENTAL SECTION

3.1. Materials. Deionized (DI) water was obtained from a Milli-Q water purification system (Synergy, EMD Millipore Corporation), which produces type I water with a resistivity greater than 18.2 M\( \Omega \)-cm at 25°C and total organic content less than 10 ppb. \( n \)-Hexadecane (99.9%) from Fisher Scientific was used as received. Triethoxy(octyl)silane, 97% from Sigma-Aldrich, was used. The measured water
surface tension was 72.8 dyne/cm, obtained using optical tensiometer (ramé hart 590), and the viscosity of water was 1 mPa s measured using an Anton Paar RheolabQC rotational rheometer at 25 °C. The capillaries used were made of borosilicate glass from VitroCom. 0.2 μm nylon syringe filters were used to remove any suspended particles in the fluids used in the coating process. The used substrate, whether borosilicate glass capillaries, flat glass slides, or silicon wafers, was cleaned through the following steps. First, the substrate was immersed in acidic Piranha solution (a 3:1 mixture of sulfuric acid and 30% hydrogen peroxide) for 10 min, followed by DI water rinsing and purging with N6.0-grade nitrogen. The substrate was stored under DI water. Just before starting the coating process, the substrate was put in an oven placed in a plasma chamber for 15 min to activate the surface. A picolow-pressure plasma system (Diener electronic, Germany) was used at 13.56 MHz generator frequency and 10% of the maximum power of 200 W. The chamber was first vacuumed down to 0.3 mbar, and then, plasma was ignited while oxygen was injected at a rate of 10 sccm for 15 min.

3.2. Coating Methodology and Characterization. Out of several available coating options published in the literature, we chose the silane method.5,6,53 This is a well-established procedure that gives reproducible results. Typically, a solution of a silane ethoxy/methoxy derivative is used in an organic solvent, like toluene. The choice of toluene is optimal because of its reasonable but limited miscibility with water, which is required to initiate the coating reaction. However, the presence of excess water leads to fast polymerization of silane and failure of the procedure. In our capillary coating procedure described below, which uses water to mask part of the capillary surface, toluene is a poor choice as water is present in relatively high quantity in our system, resulting in fast polymerization of the coating chemical and clogging of the capillaries. Consequently, we changed toluene to a more suitable and safer solvent, hexadecane, which exhibits lower water miscibility. For the same reason, we chose triethoxysilyl)silane (TES) as the coating chemical. Such a long-chain alkaline silane is preferred in our system because chlorine and amine silanes are sensitive to water and polymerize very fast in the presence of humidity. More details of the silanization process are presented in Supporting Information, Section S3.

A reliable coating procedure of flat surfaces must be developed and evaluated before embarking on the challenging task of coating square glass capillaries in a mixed-wet fashion. We evaluated the coating deposited from hexadecane using silicon wafers that were submerged half into water and half into a 1% TES solution in hexadecane. The clean wafer is dipped vertically first into water to cover the lower half of the surface. Next, oil is poured gently on top to cover the other half. The TES coating quality and the water masking efficiency appear as the sharpness of the boundary between regions of masked and non-masked regions. Using this approach, we were able to evaluate our coating procedure in a mixed solvent system.

Figure 2a shows two droplets of the same volume deposited at different spots of the same silica wafer. The left side of the wafer was exposed to TES solution in hexadecane, whereas the right side of the wafer was masked by the aqueous phase. An optical tensiometer (Biolin Theta Flex TF300) was used to measure the water/air contact angle that the droplets adopted on the surface. There is a clear difference in contact angles and areal coverage between the coated (103°) and non-coated (25°) sides of the wafer. The TES static contact angle of about 103° is in agreement with the literature values.54 Similar values of contact angles were obtained on borosilicate glass substrates (the material of the capillaries) using the above coating procedure. Figure 2b shows a bird’s eye view of the wafer surface that was sprayed with water mist using a portable humidifier. A clear and sharp boundary between the coated and non-coated areas is noticed. The droplet diameter is another major difference between the two sides as they spread more on the water-wet side. The slight curvature of the boundary is due to the coating procedure specifics (see Supporting Information, Section S5).

In order to evaluate the coating consistency and sharpness of the mixed-wet boundary at a microscopic level, atomic force microscopy (AFM) microscopy was employed. Our experiments were conducted using a Bruker Dimension Icon model (Bruker Corporation, Massachusetts, CA, USA) in the force modulation mode. Post-processing and visualization of the data were performed using Gwyddion software.55 Figure 2 shows topography (c) and AC signal amplitude (d) scans of the mixed-wet-coated silica wafer. The topography image does not show distinct changes between the coated and non-coated sides of the substrate. The calculated root mean square roughness for the two regions is very close, with 828 and 922 nm, as assessed for the AC signal amplitude values, which is expected for a “softer” surface, like a silane coating.56 In addition, we used X-ray photoelectron spectroscopy (XPS) and environmental scanning electron microscopy (ESEM) to analyze the composition of the coating and further evaluate its quality on a microscale (see Supporting Information, Sections S5.2 and S5.3). We conclude that the coating is of high quality, uniform, and has a sharp boundary transition between the coated and non-coated domains and that the surface masking with the aqueous phase is successful.

3.3. Mixed-Wet Coating of Angular Capillaries. Mixed wettability in angular capillaries is achieved by masking their corners from TES to prevent surface modification. To our knowledge, this is the first example of fabrication of reservoir-representative mixed-wet capillaries. The coating process mimics what happens in nature during crude oil primary drainage of a reservoir, as presented in Figure 1. First, the water-wet capillaries are pre-filled with deionized water (wetting phase) followed by slow injection (2−3 μL/min) of a 1 wt % solution of TES in hexadecane (non-wetting phase). At this slow injection rate, the non-wetting phase displaces water from the center but cannot completely drain the corners of the water-filled channel. After the drainage process is complete, some volume of water is kept at the end of the capillary to replenish the corner filaments (or films). The capillaries are left exposed to TES/hexadecane solution overnight at room temperature. They are then rinsed with toluene and acetone, followed by rinsing with DI water. Finally, the coating is cured in an oven under a house vacuum of about −30 mm-Hg at 120 °C for 10 min. A layout of the coating setup and other experimental details can be found in Supporting Information. Characterization of the coating of the inner walls of a capillary is challenging. Because of glass imperfections and roughness toward the corner vertex, direct in situ methods, such as AFM, which can give direct confirmation, cannot be used. Therefore, we rely on a combination of indirect methods, including capillary rise and flat surface evaluation as described before, to validate the coating procedure. We confirm below that the walls away from corners of the mixed-wet capillaries are indeed oil-wet.

We use confocal laser microscopy to determine the extent of the masked area inside the capillary. Figure 3a shows a reconstructed 3D image of the corner filaments established after hexadecane drained water from the inside of a 1 mm-wide square capillary, leaving the residual water filaments in the corners (only the top half of the capillary is shown). A laser line of 488 nm wavelength was used, and the water was stained with fluorescein dye. The filaments mask the wall surface across about 180 μm on each side. The boundary of the corner films is sharp at a resolution of 1 μm.

As another proof of concept, we performed capillary drainage experiments on oil-wet (fully coated), mixed-wet, and fully water-wet (O, plasma-cleaned and non-coated) square capillaries. The fully oil-wet capillaries are coated following the same procedure as the mixed-wet capillaries, except that they are initially completely dry. Therefore, the corners are not masked, and surface modification occurs throughout the entire surface of the capillary. Figure 3 shows three respective capillaries ordered from left to right that were initially filled with dyed water (fluorescein). The capillaries were held vertically and then lowered to touch a horizontally placed filter paper that drains liquid out of the duct. In the case of a fully oil-wet duct (b) with a static contact angle of around 103°, no corner films were observed. As
expected, water corner filaments were left behind in the case of the fully water-wet capillary (d). The mixed-wet case (c) showed remaining corner films as well. We conclude that the corners in the mixed-wet capillaries are indeed water-wet.

### 3.4. Dynamics of Capillary Invasion

Capillary imbibition experiments have a long history using different liquids, geometries, and capillary orientations. In our experiments, we focus on vertical capillary rise with water and air as wetting and non-wetting fluids, respectively.

In our experiments, the capillary is held vertical with a right-angle clamp while a large-diameter Petri dish full of the imbibing liquid to be tested is slowly raised using a laboratory jack (Thorlabs, L490) until the fluid surface touches the inlet of the capillary. A Phantom V2640 high-speed camera captures the meniscus rise. A diffuser and a back white light source are used to provide uniform back illumination (see Supporting Information). With this setup, we experimentally study the spontaneous invasion into mixed-wet capillaries and compare it with invasion into fully water-wet and fully oil-wet (fully coated) square capillaries. Captured images are converted to a binary format using thresholding, and the interface is tracked as it advances in time using a MATLAB code. In the following section, we compare our experimental findings with the predictions of theoretical models and discuss the similarities and differences between them.

### 4. RESULTS AND DISCUSSION

#### 4.1. Invasion into Uniformly Water-Wet Capillaries

First, we validate our experimental method and establish the theoretical model that best describes the simple case of water imbibition into a uniformly fully water-wet circular capillary. The dynamics of the rise are very fast, such that the experiment had to be recorded at a high speed of 1000 fps. The results are presented in Supporting Information, Figure S9. All models describe well the late-time dynamics, while early dynamics differentiate the models. We find that the Szekely model, eq 7, which accounts for inertia, describes the early rise dynamics accurately. This is consistent with the previous studies which show that no inertia in the Washburn leads to a faster rise than experimental data, especially for low-viscosity fluids. We conclude that our experimental approach used with fully water-wet cylindrical capillaries yields realistic experimental data that are well reproduced using the Szekely model.

Next, we discuss meniscus rise in the uniformly water-wet square capillaries. In this experiment, there is no residual wetting fluid pinned in the corners as the capillaries are completely dried before use. According to eq 11 in the MSP theory section above, this dried case is analogous to primary drainage up to infinite capillary pressure that leads to zero residual water saturation. In our experiment, the non-wetting fluid is air. The water imbibition process here (i.e., capillary rise) is the inverse of drainage, with the advancing contact angle replacing the receding angle when a terminal meniscus imbibes into a pore that initially contains a non-wetting phase. Thus, for a fully water-wet capillary, water imbibition or rise occurs spontaneously, as expected from MSP theory (eq S18), because an advancing contact angle will be attained immediately on such a surface ($\theta_a \approx 0^\circ$ after plasma cleaning of glass). Therefore, MSP theory prediction is consistent with the experimental observation (Figure 4).

![Figure 4](https://doi.org/10.1021/acs.energylett.2c00236)
capillaries were plasma-cleaned in an oxygen atmosphere just before each experiment. The final rise height corresponds to zero frontal velocity as the flow stops when the viscous and inertial forces vanish, while the opposing force of the liquid column weight balances the interfacial force. The final rise height, obtained by solving eqs 3, 4, and 7, is 3.1 cm. Yet, there is a small discrepancy between the models and the experimental data due to the fact that none of the models fully captures the physics of the process, that is, corner rise. Indeed, the rise of the MTM in the square capillaries is accompanied by rise of corner (or arc) menisci that could change the MTM curvature and thus the capillary pressure and the final height. Such a corner rise behavior has been observed in previous studies, and its description lies outside of the scope of our work.62,66 However, the dynamics of MTM rise in a uniformly wet square capillary could still be captured decently using the considered models of circular capillaries.

Figure 4b gives a higher resolution of the early dynamics on a dimensionless scale that compares the MTM rise data and the three models. Height is normalized using the capillary length, $a = \sqrt{\gamma/g\mu}$. Dimensionless time is expressed as $t' = t/\mu a$. Indeed, in Figure 4b, the experimental data, including early dynamics, are well described using the Szekely model. Figure 4c shows the slope calculated from Figure 4b versus time. Based on the experimental data, we conclude again that the Szekely model best describes the rise dynamics during water invasion into uniformly water-wet square capillaries with only a small discrepancy in the final rise height due to rise in ARs not accounted for by the models.

4.2. Impact of Wettability Alteration on Capillary Invasion. In this section, we examine water invasion into fully oil-wet and mixed-wet capillaries. Our produced mixed-wet capillaries, about 180 μm from both sides of each corner, remain water-wet (Figure 3a). The remaining inner surface of the capillaries is made oil-wet. This situation corresponds to some residual water saturation (water left in the corners), which in a subsurface oil reservoir depends on the capillary pressure at the end of primary drainage.

The residual water saturation in the mixed-wet capillaries used in this experiment was gravimetrically measured to be $\pm 4.6\%$, while the fully oil-wet capillaries had no residual water. The residual saturation was obtained by filling the whole capillary with water and then draining the water using a filter paper as shown previously in Figure 3, leaving some water trapped in the water-wet corners.

Figure 5a compares on linear scales the experimentally observed rise height of MTM in the mixed-wet and oil-wet (fully coated) square capillaries, with the three dynamic models used above. The advancing contact angle of the coated surfaces was measured to be $\sim 107°$ (see Supporting Information, Figure S8), yet we observed spontaneous imbibition in the mixed-wet capillaries case with a saturation of $\pm 4.6\%$. In contrast, no rise was observed in the fully coated oil-wet capillaries that had a water saturation of $\pm 0\%$. The water content is represented by the areal saturation of the cross-section. It is interesting to note that due to the phenomenon of the dynamic contact angle, we miss a few experimental data points in Figure 5a, just before the MTM reaches its highest position. At this point, the dynamic contact angle is close to 90°. The meniscus becomes almost flat, leading to no refraction of light, lack of contrast, the two phases become indistinguishable, and we lose track of the interface in image processing. A final rise height of 72 mm is observed in the case of mixed-wet capillaries, which is intermediate between fully coated (zero) and fully water-wet (320 mm) (Figure 4a). For the three dynamic models, the final rise height was matched with the experimental value by tuning the contact angle as an input parameter. The final height corresponds to an apparent contact angle of $77°$, with all other parameters (i.e., surface tension, viscosity etc.) being the same as in the above calculations. This angle can be considered as a form of Cassie’s apparent contact angle of heterogeneous surfaces.11,12

For imbibition to occur in such a mixed-wet configuration, the three-dimensional, concave MTM can only proceed if it makes a contact angle equal to $\theta_c$ with the central parts of pore walls that were exposed to oil and changed wettability, as depicted in Figure 1, or if it merges with the corner water swelling inside a pore. For large $\theta_c \geq 90°$, MTM advancing on an oil-wet surface would result in a convex interface and imbibition would have to be forced. Therefore, where MTM contacts AMs, it must merge with them seamlessly. In other words, corner water in contact with MTM has to swell and rearrange by sucking in water from the MTM for spontaneous invasion to occur. This would have to be an extremely fast, dynamic process. Work is ongoing to capture the dynamics of such a process using fast 3D laser sheet imaging.

Figure 5b,c shows on a log–log scale, dimensionless rise height and slope versus dimensionless time for a mixed-wet square capillary. Even though the very first points are not far from the predictions of Bosanquet and Szekely models, as time progresses, the experimental data deviate from the predictions. Moreover, the two models overshoot the equilibrium height and then return to it. Oscillations in capillary rise have been previously observed experimentally and numerically for some low-viscosity fluids.
Our results are in agreement with the predictions of MSP theory of imbibition, as shown in Figure 6, obtained by solving eqs 10 and 11. Figure 6 shows the maximum advancing contact angle, $\theta_{a,max}$ values for spontaneous imbibition to occur inside capillaries of square geometry at different values of residual water saturation, $S_w$. $\theta_{a,max}$ corresponds to zero capillary pressure at which the imbibition ceases to be spontaneous. With water saturation of about $\approx4.6\%$, $\theta_{a,max}$ is about 125°. Hence, MSP correctly predicts imbibition to be spontaneous in our mixed-wet capillary with $\theta_r \approx 107^\circ$. On the contrary, for a fully coated capillary with $S_w \approx 0\%$, the maximum advancing angle is 90°. Therefore, with $\theta_r \approx 107^\circ$, MSP predicts that no spontaneous imbibition can take place, as observed experimentally. The curve is bounded from the right by the water saturation corresponding to the dimensionless entry capillary pressure in drainage, which is equal to 1.89 for a square cross-section duct. The receding angle $\theta_r$ used in the MSP calculation is 0° as the capillaries were perfectly water-wet prior to the coating due to O2 plasma cleaning.

The results confirm that the MTM can still slide on the oil-wet films, and therefore, imbibition can be spontaneous, even for surfaces with advancing contact angles higher than 90°, given the presence of the correct amount of residual water in the corners or reduction of the advancing contact angle beyond a certain threshold value. As we see from figure 6, less tendency to be wet by water results in higher requirement of residual water saturation for imbibition to occur. We are currently working on studying the impact of brine composition on the physico-chemical properties of the interfacial films responsible for wettability alteration.19

5. CONCLUSIONS

This contribution presents a new selective silane coating approach for fabricating reservoir-representative mixed-wet capillaries with square cross-sections. The coating quality and uniformity are assessed on a microscopic scale using AFM, XPS, and ESEM. Additionally, a macroscopic-scale evaluation is conducted with capillary drainage and contact angle measurements using optical tensiometry. These complementary investigations confirm the high quality and uniformity of the resulting coating and the masked areas. The presented method has the potential to be extended to microfluidic devices to study flow dynamics in multi-channel systems.

Capillary rise experiments were conducted to evaluate dynamics of two-phase fluid flow in the fully water-wet, fully oil-wet, and true mixed-wet (not to be confused with partially wet) capillaries. We find that the Szekely dynamic model adequately describes the capillary invasion in uniformly water-wet capillaries. However, the observed flow dynamics in mixed-wet capillaries is different from that in the uniformly wet ones with an equivalent averaged contact angle. Therefore, the investigated dynamic capillary invasion models fail to capture the flow behavior in a mixed-wet setting. Furthermore, theory development is required to correctly capture pore-scale flow dynamics in mixed-wet media.

Our experiments in mixed-wet capillaries confirm the possibility of spontaneously invading oil-wet angular pores with advancing contact angles larger than 90°, given the presence of water-filled hydrophilic corner regions. Spontaneous imbibition can be promoted by lowering the advancing contact angle below a critical value established from MSP theory (still larger than 90°). The threshold angle is a function of pore geometry, residual water saturation, and receding contact angle. To the best of our knowledge, this is the first direct experimental confirmation of the quasi-static MSP theory in mixed-wet pores in such a controlled manner and on such a scale. Our findings are guiding research on increasing oil recovery from microporous rocks. Indeed, even small changes in the advancing contact angle can promote spontaneous brine imbibition, resulting in higher oil recovery. Such contact angle changes can be achieved by affecting crude oil–brine–rock interactions via injected brine chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c00236.

More details and derivations of the MSP formulation for drainage, imbibition, and the maximum advancing contact angle, more experimental details of the mixed wet coating technique and its evaluation using ESEM, XPS, and contact angle measurement, and additional results of capillary rise dynamics (PDF)

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