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Pore wall rugosity: The role of extended wetting contact line length during spontaneous liquid imbibition in porous media

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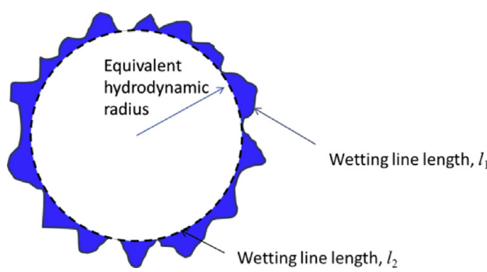
HIGHLIGHTS

- The two experimentally discrete liquid imbibition rate regimes were discussed.
- A wetting and an imbibition model based on pore wall rugosity were proposed.
- An experimentally characteristic wetting line length was measured and confirmed.
- The imbibition rate on both initial timescale and longer timescale was predicted.

GRAPHICAL ABSTRACT



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ABSTRACT

Considering the separable phenomena of imbibition in complex fine porous media as a function of timescale, it is noted that there are two discrete imbibition rate regimes when expressed as a function of the square root of time using the traditional Lucas–Washburn equation. Commonly, to account for this deviation from uniform absorption into a single equivalent hydraulic capillary, many experimentalists propose an effective contact angle change. Such an assumption, however, challenges the consistency of constant surface energy and is difficult to justify physically. In this work, we consider rather the general term of the Wilhelmy wetting force in respect to the Washburn wetting line length, and apply a proposed increase in the liquid–solid contact line length provided by the introduction of surface meso and nanoscale rugosity in respect to the pore wall roughness. The experimental characteristic wetting line length is here defined via a relation between capillary condensation area, as measured independently using nitrogen gas (BET surface area determination plus BJH hysteresis analysis), and an equivalent capillary length containing the known saturation absorbed liquid volume. This model, constructed by applying the extended wetting contact line length to the equivalent hydraulic capillary observed at the longer timescale II imbibition, is applied for the initial timescale I imbibition rate whilst keeping the imbibition volume of the equivalent capillary tube constant. The longer timescale II imbibition is then subsequently defined traditionally by the smooth-walled equivalent hydrodynamic capillary, in which the surface rugosity is prefilled via a precursor liquid film supported further by liquid vapour condensation within the pore wall surface meso/nano-roughness. This two-stage model is compared with experimental liquid absorption data from a ground calcium carbonate porous compact and shown to provide good agreement. Using this concept, it is possible to unite the process of imbibition in complex porous media with a single equivalent

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hydraulic radius and an experimentally justified extended wetting line length to predict the imbibition rate of porous media on both the initial and longer timescales in cases where the imbibed liquid mass is low and the nano and microcapillary pressure of fine pore media far exceeds the effect of gravity.

1. Introduction

The imbibition of a wetting liquid into a porous medium is an important frequently occurring phenomenon in both natural and industrial systems, as seen, for example, in soil science, petroleum recovery science, the papermaking and printing industries, and in the constructional materials industry. The earliest approach for describing imbibition dynamic was proposed by Bell and Cameron [1] and Ostwald [2], who found a dependency of absorption volume on the square-root of time ($\sqrt{t}$). The analytical equation and its solution were then presented by Lucas [3] and Washburn [4] by means of balancing the Laplace meniscus pressure relation with Poiseuille's equation of viscous resistive laminar flow, which is well known as the Lucas–Washburn (L–W) equation.

$$x^2 = \left(\frac{R_{\mathrm{ehc}} \gamma_{\mathrm{LV}} \cos\theta}{2\eta} \right) t \tag{1}$$

where x is the distance travelled by the liquid with viscosity, η, undergoing imbibition in a horizontal capillary of radius R_{ehc}, representing the equivalent hydraulic (hydrodynamic) capillary of the sample, with a wetting force given as the liquid surface tension, γ_{LV}, in contact with the solid surface having a meniscus boundary angle of θ.

Attempts to explain observed deviation from this standard imbibition model, based on the single equivalent hydraulic capillary, have received increasing attention, with exploration of several alternative models [5]. Frequently, the inertial effect is invoked as missing in the L–W equation, a point recognised and stressed by Rideal in 1922 [6]. On the basis of Rideal's research, Bosanquet [7] in his equation of 1923 added the inertial impulse drag effect associated with an accelerating fluid to complement the Poiseuille flow, expressed in the case where no external pressure is applied, as

$$\frac{d}{dt}\left(\pi R_{\mathrm{ehc}}^2 \rho x \frac{dx}{dt} \right) + 8\pi\eta x \frac{dx}{dt} = l \gamma_{\mathrm{LV}} \cos\theta \tag{2}$$

Eq. (2) introduces the wetting line length, l (which for the simple cylindrical capillary = $2\pi R_{\mathrm{ehc}}$) and the liquid density, ρ, required to consider the inertial impulse effect. Later, researchers attempted to describe a real porous liquid-imbibing system by adding further refinements based on the Bosanquet equation by a variety of methods, including substituting the discontinuity in the Bosanquet rate equation at $t = 0$ with capillary entrance energy loss [8], but the results eventually showed that they were either equivalent to that of Bosanquet or to be analytically unmanageable due to the number of unknown parameters when applying them to a realistic porous medium [9,10].

In practical application, the Bosanquet equation was not widely accepted compared with the traditional Lucas–Washburn equation. This was partly due to Bosanquet's own application for the concept to a single capillary, himself explaining that the inertial effect was too short lived to be of importance. As a result, many researchers thought the impact of inertia on imbibition to be negligible because of its influence only over very short time during initial imbibition. Though this is true in general for the single capillary case, or when studying the imbibition process on a longer timescale for some highly viscous and/or poorly wetting liquids, those who rejected the concept overlooked the continuous acceleration and deceleration effects at the wetting front in a complex geometry network structure. Thus, the cumulative effect of inertia should not be ignored in an interconnected network structural material, and is required as an integral part of the physics when analysing the process of dynamic forces acting during imbibition at the wetting front, although the decay of imbibition rate from linear t to $\sqrt{t}$ is intrinsic to the eventual dominance of viscous drag within the saturated medium behind the wetting front. Thus, comparing the L–W and Bosanquet equations, it is readily identifiable that the Bosanquet equation relaxes to the general form for the L–W equation as t increases. Gane et al. [11], Schoelkopf et al. [12] and Ridgway et al. [13] highlighted this aspect, and established the expression of complexity of a porous network based on the coating material structure analysis of fine printing paper. The same workers then further expanded their model application to other materials, like medicinal tablets, sand and building materials, providing reasonable correlation with the important first phase of liquid absorption and describing the selective pore filling phenomenon in terms of a preferred pathway of wetting.

The expression for Bosanquet is more complicated than the L–W equation, and in fact discontinuous at the instance of first absorption, such that solutions can only be approximated at the initial timescale limit of the acceleration operator, $\lim_{t\to 0} d^2/dt^2$. Researchers, therefore, would often prefer to attempt some modification without invoking such complexity, so as to enlarge the range of applicability of the L–W equation in the early process of imbibition. Hammecker and Jeannette [14] and Leventis et al. [15] modified the L–W equation considering microscale structural parameters, but the predicted model still showed some deviations from the experimental results, which were thought to have arisen from the profoundly complicated and irregular structure inside practical porous media. Many researchers went on to point out that the interior structural parameters of porous media, such as roughness, specific surface area, effective capillary force [16] and apparent contact angle [17], all play an important role in the imbibition, in which roughness was suspected more than other structural parameters to provide the dependence being sought to explain the faster than expected absorption. Rabinovich et al. [18] experimentally demonstrated the fluctuation of capillary forces with relation to nanoscale features, which increased gradually with increasing roughness, and Stukan et al. [19] investigated the spontaneous imbibition of liquid in nanopores with different roughness resorting to molecular dynamic simulation to match the L–W equation. Dimitrov et al. [20] provided the molecular dynamics evidence for roughness (coarse-grained) models of nanotubes in a nanopore construct with a further modified L–W equation, adding the slip length, which effectively matches the Bosanquet plug flow solution ($\lim t \to 0$). The work of Bico et al. [21] and Quéré [22] in turn discussed the wetting of textured surfaces, providing a quantitative description of the changes of contact angle during the wetting, and indicated that the apparent contact angle for super-hydrophilic solids is greater than that of Wenzel's contact angle correction. The primary reason for this can be understood as a smoothing effect of the liquid film covering the nano textured surface, which erases the solid roughness seen at the initial stage of wetting, in the bulk over time. This kind of film is formed by surface flow and capillary condensation [23] in the meso and/or nanoscale surface pores constituting the roughness. A parameter defining roughness of a pore surface could, therefore, be seriously considered when initial wetting and imbibition are proceeding in a complex porous medium, as the roughness alters the Wilhelmy contact wetting line length.