Characterization of Porous Media by the Kinetics of Liquid Penetration: The Vertical Capillaries Model

Abraham Marmur and Ruben D. Cohen

Department of Chemical Engineering, Technion—Israel Institute of Technology, 32000 Haifa, Israel

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INTRODUCTION

The characterization of the structure of porous media is an important practical need in relationship with many processes and applications. A few well-known methods of characterization exist (e.g., 1–7), by which parameters of the geometrical structure of the porous medium are calculated from equilibrium measurements based on the Young–Laplace equation. In most of these methods, the contact angle needs to be a priori known or estimated, however under proper conditions the contact angle may be sometimes elucidated as well (2, 3).

The main interest in many practically important applications is in the kinetics of penetration of liquids into porous media rather than in the final equilibrium state. Theoretical models which relate the kinetics of penetration to the structure of a porous medium, as elucidated by the above-mentioned static measurements, are still deficient. Therefore, it may be advantageous to characterize porous media directly by measuring the kinetics of penetration. Such measurements may furnish the characteristics most pertinent to the penetration process. Obviously, in order to interpret the results of such experiments, theoretical models are also required; therefore, it may seem that kinetic measurements do not solve the problem of theoretical deficiency. However, at the current state of knowledge, it is more practical to fit simplified models to experimental data for the kinetics of penetration than to a priori predict this kinetics based on data of the structure of the medium.

The simplest theoretical model which can be used is the well-known Lucas–Washburn equation (8, 9) for the penetration of a liquid into an empty horizontal cylindrical capillary,

\[ x^2 = \frac{\sigma r \cos \theta}{2\mu} t, \]  \[ \text{[1]} \]

where \( x \) is the distance penetrated by the liquid, \( \sigma \) is the surface tension of the liquid, \( \mu \) is its viscosity, \( \theta \) is the contact angle between the liquid and the inside surface of the capillary, \( r \) is the internal radius of the capillary, and \( t \) is the time. This equation has been tested over the years (10–12) and has been used to characterize porous media by calculating \( r \cos \theta \) from the slope of the curve of \( x^2 \) vs \( t \).

This approach is very useful, since it defines an "effective" capillary, the kinetics of penetration into which is the same as for the real porous medium. However, the main deficiency of this approach, as can be concluded from Eq. [1], is the fact that only the product \( r \cos \theta \) can be elucidated and not \( r \) or \( \cos \theta \) separately. In other words, the characteristic size of the pores cannot be estimated independently of the wetting properties of the system. In many cases it was assumed that \( \cos \theta = 1 \), but this may be erroneous, as will be demonstrated and discussed below.

A solution to this problem is offered by performing and
analyzing vertical penetration experiments, since the equations developed by Lucas and Washburn (8, 9) show that \( r \) and \( \cos \theta \) can be separately evaluated from the results of such experiments. The first goal of this paper is to present an alternative way of presenting the well-known solution for a single vertical cylindrical capillary, which can be useful for the purpose of characterization of porous media.

The next step in modeling penetration into a porous medium is to treat the latter as an assembly of cylindrical capillaries of various radii and the same contact angles. Therefore, the second goal of this paper is to present an equation for the kinetics of the advancement of the front of the liquid in such an assembly. As will be shown, this equation can be regarded as a natural extension of the approach taken here toward the presentation of the kinetics of penetration into a single vertical capillary.

**THEORY**

**Single Vertical Cylindrical Capillary**

The basic model for capillary rise in a vertical capillary was independently developed by Lucas and Washburn (8, 9). For a capillary which initially contains a fluid of negligible viscosity (usually a gas) it can be written in the manner

\[
At = -Bh - \ln(1 - Bh),
\]

where

\[
A = \frac{\rho^2 g^2 r^3}{16 \sigma \mu \cos \theta},
\]

\[
B = \frac{\rho g r}{2 \sigma \cos \theta},
\]

\( h \) is the height of rise of the liquid, \( \rho \) is the density difference between the liquid and the fluid, and \( g \) is the gravitational acceleration. Equation [1] ignores the effects of inertia, which may be especially important for the initial stages of penetration (13–20). However, it was shown that this equation accurately describes the kinetics of penetration for a capillary of sufficiently small internal radius (21).

From Eq. [2] it is clear that \( r \) and \( \cos \theta \) independently contribute to vertical capillary rise, unlike the case of horizontal penetration for which they always appear as the product \( r \cos \theta \). Therefore, the advantage of performing vertical penetration experiments is clear. The problem is to find the best way to present and analyze the data. One possibility is to take advantage of the fact that a plot of \( [-Bh - \ln(1 - Bh)] vs t \) must be linear, according to Eq. [2], regardless of the value of \( A \). This possibility can be materialized by varying \( B \), in search of the value of \( B \) which makes the above-mentioned plot most linear (highest correlation coefficient). The slope of this best line gives the best estimate of \( A \). This method may be useful if indeed the single capillary model is adequate for the system under study. In fact, as will be demonstrated below, this approach may be used to decide whether the single capillary model well describes a particular system.

Another possibility, which, as will be shown below, naturally leads to the capillary assembly model, is indicated by Eq. [2] when it is rewritten in a form of an infinite series of dimensionless terms:

\[
1 = \frac{B^2}{A} \frac{h^2}{t} + \frac{B^3}{A} \frac{h^3}{t} + \frac{B^4}{A} \frac{h^4}{t} + \cdots.
\]

It turns out that the coefficient of \( h^3/t \),

\[
\frac{B^3}{A} = \frac{2 \rho g \mu}{\sigma^2 \cos^2 \theta},
\]

is independent of \( r \). This suggests that a plot of \( h^3/t \) vs \( t \) may be useful in distinguishing between the effect of \( r \) and the effect of \( \cos \theta \).

Based on this idea, the dimensionless function \( (Bh)^3/(At) \) was plotted vs \( At \), as shown in Fig. 1. The values of \( Bh \) which were used for this plot were calculated from Eq. [2]. Since the latter is a universal equation, so is the plot of \( (Bh)^3/(At) \) vs \( At \). A simple numerical investigation reveals that the maximum in \( (Bh)^3/(At) \), which is demonstrated in Fig. 1, is given by

\[
\left. \frac{(Bh)^3}{At} \right|_{\text{max}} = 0.68692.
\]

![FIG. 1. Dimensionless height of rise in a single vertical cylindrical capillary vs dimensionless time.](image-url)
An Assembly of Vertical Cylindrical Capillaries in Parallel

The model of an “effective” single cylindrical capillary is the simplest possible model to describe capillary penetration into a porous medium. Obviously, this model may be insufficient in many cases, especially when a significant distribution of pore sizes exists. The next step is, therefore, to model a porous medium as an assembly of cylindrical capillaries of various radii, which are characterized, however, by the same contact angle. The latter assumption is not obvious, but it may serve as a first approximation. Moreover, as will be shown below, the proposed model enables examination of the suitability of this assumption.

In a capillary penetration experiment with a real porous medium, the most readily observed parameter is the upper front of the penetrating liquid. In the capillary assembly model, the upper front of the penetrating liquid corresponds, at any given moment, to the maximum height of liquid among all capillaries in the assembly. The initial rate of penetration is higher for the wider capillaries in the assembly, however, the final height of rise in them is smaller. Therefore, the upper liquid front initially represents the widest capillaries, and then the smaller capillaries gradually take over, according to the specific radius distribution in the assembly.

Assuming for the moment a continuous distribution of capillary radii, the maximum height at any given time can be calculated by imposing on \( h(r) \) the following condition:

\[
\left( \frac{\partial h}{\partial r} \right) = 0. \tag{9}
\]

The relationship \( h(r) \) is derived from Eq. [2] by explicitly writing the radius \( r \) instead of including it in the constants \( A \) and \( B \).

The maximum occurs at a time given by

\[
At|_{\text{max} h \neq 0} = 0.39066. \tag{8}
\]

The numerical values given in Eqs. [7] and [8] are also universal, due to the universality of the plot. Since \( B^3/A \) is independent of the capillary radius, it turns out that the maximum in \( h^3/t \) is also independent of \( r \). However, the time at which the maximum occurs does depend on \( r \), because \( A \) depends on it. Since both \( B^3/A \) and \( A \) depend on the contact angle, the latter affects the maximum in \( h^3/t \) as well as its timing. Equations [7] and [8] may then be used directly to determine \( A \) and \( B \) from experimental data, if the time and the height of the maximum in \( h^3/t \) are measured with sufficient confidence.

\[
A' = \frac{B'h}{r^2} - \frac{1}{r^3} \ln(1 - B'rh), \tag{10}
\]

where \( A' = A/r^3 \) and \( B' = B/r \). By taking the derivative of each side of this equation with respect to \( r \), remembering that \( t \) should be held constant (therefore the derivative of the left-hand side is zero), and introducing the condition given by Eq. [9], the following equation results,

\[
2y + \frac{y}{1 - y} + 3 \ln(1 - y) = 0, \tag{11}
\]

where \( y = B'rh_{u} \), \( h_{u} \) is the height of the upper front (the maximum liquid height among all capillaries), and \( r_{u} \) is the radius of the capillary in which the height of liquid is maximum. Equation [11] is solved numerically to yield

\[
y = B'r_{u}h_{u} = 0.64501. \tag{12}
\]

To get the time dependence of \( h_{u} \), this value of \( y \) is introduced into Eq. [10], to first get the time dependence of \( r_{u} \):

\[
A'r_{u}^3t = 0.39066. \tag{13}
\]

Dividing the cube of Eq. [12] by Eq. [13] one gets the desired time dependence of the upper front in the capillary assembly:

\[
\frac{(B'r_{u}h_{u})^3}{A'r_{u}^3t} = \frac{(Bh_{u})^3}{At} = 0.68692. \tag{14}
\]

It should be noticed that \( A \) and \( B \) can be used in Eq. [14] without referring to any specific capillary, since \( B^3/A \) is independent of the capillary radius and the contact angle is assumed to be the same for all capillaries. It is also useful to notice that Eqs. [12]–[14] are universal, in the same sense as Eqs. [7] and [8].

Equation [14], which gives the position of the liquid front in the capillary assembly, looks exactly the same as Eq. [7] for the maximum in \( (Bh^3)/(At) \) for a single vertical capillary. This formal identity between the two equations is best explained by following the individual curves for the capillaries in an assembly, as shown in Fig. 2 for an arbitrary discrete distribution of capillary radii. The ordinate for all the curves, \( (Bh^3)/(At) \), is the same, since the capillaries differ from each other only in their radius and \( B^3/A \) is independent of the radius. However, the abscissa must be different for each capillary to show the real time evolution; therefore the abscissa is based on the \( A \) value of one of the capillaries, say, \( A_{1} \).

The curve furthest to the left in Fig. 2 represents the largest capillary (which is ten times larger in radius than the smallest capillary in this specific example). According to
EXPERIMENTAL

Simple experiments of capillary rise in filter paper were performed. The system consisted of a filter paper strip, about 2.5 cm wide and 56 cm long, hung vertically from a clip, with its lower end pulled by the weight of another clip and dipped into a liquid container. The height of rise of the liquid at the center of the strip above the liquid level in the container was followed with time. Time zero was the moment of dipping the paper into the liquid container.

The filter paper types used were Whatman filter paper No. 1 and No. 4. The liquid used was Brookfield viscosity standard, the properties of which, at 20°C, are: viscosity, 106 cP; density, 0.9705 g/cm³; and surface tension, 21.75 mN/m. The liquid was found to be practically nonvolatile: about 0.13% of the liquid vaporized in 21 days.

RESULTS AND DISCUSSION

Two cases are discussed to demonstrate the theoretical approach presented above. The first is the capillary rise of a liquid (Brookfield viscosity standard) in Whatman filter paper, for which the analysis shows that the single capillary model is sufficient. The second case is the rise of paraffin oil in sand (22), for which the single capillary approach is insufficient, but the capillary assembly approach may be adequate.

Figure 3 shows data for the rise of the Brookfield viscosity standard in two types of Whatman filter paper, No. 1 and No. 4. The data are presented, as discussed in the theory section, in the form of \( \frac{(Bh)^3}{At} \) vs \( t \). The lines shown in the figure represent the best of all possible fits of straight lines to the data. As seen in Fig. 3, excellent fits were indeed achieved, as indicated by the very high correlation

\[
\begin{align*}
E_0 &= \frac{0.39066}{A_t} \leq t \leq \frac{0.39066}{A_s}, \\
E_t &= \frac{0.39066}{A_t} \leq t \leq \frac{0.39066}{A_s},
\end{align*}
\]

where \( A_t \) and \( A_s \) are the values of \( A \) corresponding to \( r_t \) and \( r_s \), respectively. For \( t < t_t \) or for \( t > t_s \) the height of capillary rise follows the individual curve of the largest or smallest capillary, respectively.

FIG. 2. Dimensionless height of rise in a few single vertical cylindrical capillaries of various radii vs dimensionless time. The time is made dimensionless by the value of \( A \) of one of the capillaries to show the different time evolution in each of them. Note that the maximum is the same for all. The dashed line represents an assembly of such capillaries with a continuous distribution of radii.

FIG. 3. Experimental data and their fit to the theory of a single vertical cylindrical capillary for the rise of Brookfield viscosity standard in Whatman filter paper No. 1 (●) and No. 4 (■).
Therefore, it is clear that the value of the angle of the capillary walls and the intrinsic contact angle. Because of the excellent values of the correlation coefficients for the linear fit, the $h^3/t$ vs $t$ approach is expected to give very similar values of $A$ and $B$ to those reported in Table 1. For example, the experimental value of the maximum in $h^3/t$ for Whatman filter paper No. 4 is 55.63 cm$^3$/h, and it occurs at $t = 346$ h; from these values and Eqs. [7] and [8] one gets $A = 1.129 \times 10^{-2}$ cm$^{-1}$ and $B = 2.407 \times 10^{-2}$ cm$^{-1}$, which compare very well with the values reported in Table 1. The practical advantage of fitting the data in the form of $-Bh\ln(1 - Bh)$ vs $t$ is that one does not have to wait for the maximum in $h^3/t$ to occur. However, if this fit is not good, then it is advantageous to measure this maximum, as will be demonstrated later.

The most striking result is that $\cos\theta$ comes out to be far from unity, although the intrinsic contact angle may very well be close to zero for an organic liquid on cellulose fibers. This is understandable, since $\theta$ is not meant to represent the intrinsic contact angle between the liquid and the fibers; it is the contact angle that would exist in a cylindrical capillary that is equivalent to the studied porous medium in terms of the kinetics of penetration. In the equation for the kinetics of penetration, $\theta$ stands for the apparent contact angle (the angle between the tangent to the liquid–fluid interface and the main direction of motion), which serves as a means to determine the radius of curvature of the meniscus by the expression $r/\cos\theta$. In a cylindrical capillary of smooth and homogeneous walls $\theta$ coincides with the intrinsic contact angle. In an axisymmetric capillary with a changing cross section, for example, $\theta$ is the difference (or sum, depending on the definitions of the angles) of the local inclination angle of the capillary walls and the intrinsic contact angle. Therefore, it is clear that the value of $\theta$ which characterizes a porous medium is some average of the intrinsic contact angle and local inclination angles. This average may be very different from the intrinsic contact angle itself, as demonstrated in the present analysis.

To gain more confidence in the present results, the values of the product $r \cos\theta$, as obtained in the vertical penetration experiments reported here, are compared with the values obtained from studies of horizontal penetration into the same paper types (12). This is also shown in Table 1. The agreement between the $r \cos\theta$ values calculated from the two different experiments is good. This agreement emphasizes the advantage of using the vertical capillary penetration experiment: the two experiments yield the same information about $r \cos\theta$, however only the vertical penetration experiment enables the independent calculation of $\theta$.

As mentioned above, the single capillary model may be expected to fit data for capillary rise in porous media only under special circumstances. The next case to be presented here demonstrates this point. Figure 4 shows the $-Bh\ln(1 - Bh)$ vs $t$ plot for the data measured by Hackett for paraffin oil in sand (22). These data were chosen, since they seem to be the only data presented in tabular form. The straight line shown in this figure is the best possible line, from which the values of $A$ and $B$ are calculated to be $9.38 \times 10^{-4}$ h$^{-1}$ and $2.58 \times 10^{-2}$ cm$^{-1}$, respectively. However, this line does not fit the data very well, as can be seen in the figure and as implied by the value of the correlation coefficient ($R^2 = 0.955$). This is an indication that the single capillary model is insufficient in this case. It is then natural to try the next level in modeling, i.e., the assembly of cylindrical capillaries in parallel.

Figure 5 shows again the experimental data of Hackett, together with three theoretical curves, in the form of $(Bh)^{3/2}$

![Figure 4](image)

**TABLE 1**

Summary of Results for the Rise of a Liquid (Brookfield Viscosity Standard) in Whatman Filter Papers

<table>
<thead>
<tr>
<th>Whatman filter paper No.</th>
<th>$A$ h$^{-1}$</th>
<th>$B$ cm$^{-1}$</th>
<th>$r \mu$m</th>
<th>$\cos \theta$</th>
<th>$r \cos \theta \mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$6.292 \times 10^{-4}$</td>
<td>0.024</td>
<td>2.55</td>
<td>0.232</td>
<td>0.592</td>
</tr>
<tr>
<td>4</td>
<td>$1.123 \times 10^{-3}$</td>
<td>0.024</td>
<td>3.40</td>
<td>0.310</td>
<td>1.05</td>
</tr>
</tbody>
</table>

*Average of results for four organic liquids.
$A_t$ vs $A_1 t$. The dashed curve represents the theoretical curve for a single capillary, which is based on the experimental maximum point in $h^3/t$ (the data are not sufficiently detailed to exactly determine the maximum, therefore the calculation is based on the single point which shows the highest $h^3/t$). The values of $A$ and $B$ thus calculated are $5.858$ $\text{h}^{-1}$ and $0.0821$ $\text{cm}$, respectively (corresponding to $r = 1.718 \times 10^{-3}$ $\text{cm}$ and $\cos \theta = 0.3189$). This value of $A$ is used as $A_1$ in the abscissa. It should be noted that these values of $A$ and $B$ differ very much from those calculated from the fitting of a straight line. The dashed curve obviously fits the maximum, however it does not fit well the other experimental points (this is not surprising, since it has already been established that the single capillary model does not fit the data).

To fit the capillary assembly model, one needs first to fit the curves which represent the largest and smallest capillaries. It turns out (by trial and error), as shown in Fig. 5, that the curves for $r = 1.89 \times 10^{-3}$ $\text{cm}$ and $r = 1.29 \times 10^{-3}$ $\text{cm}$ (and the same $\cos \theta$ as above) fit quite well the left-hand side and the right-hand side of the experimental curve, respectively. Thus, although the experimental data are not sufficiently detailed, it seems that the present approach is able to approximately determine the range of equivalent pore radii of the sand. The sand was defined as having a mean grade of $1.68 \times 10^{-2}$ $\text{cm}$ (22). It seems quite feasible that particles of this diameter will have pore spaces characterized by diameters which are about five times smaller than those of the particles themselves.

Obviously, the capillary assembly model, which assumes the same $\cos \theta$ in all capillaries, may not be sufficient for the characterization of some porous media. However, when this is the case, the experimental data should show local maxima at different heights in $h^3/t$. Thus, the form of data presentation which is required by the present model is also useful in detecting its limitations. The model will be extended to include the effect of $\cos \theta$ when experimental data are available to test it.

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**REFERENCES**