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Quantitative measurements of capillary absorption in thin porous media by the Automatic Scanning Absorptometer

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Highlights

- ASA can be used to quantitatively measure liquid penetration in thin porous media.
- The liquid penetration depth is determined using a 1D model based on Darcy's law.
- Two transport regimes are found for liquid penetration in porous filter membranes.
- ASA measurements agree with NMR measurements on similar liquid-media systems.

Abstract

A 1D model based on Darcy’s law is proposed to allow quantitative measurements of the penetration depth of water-glycerol-hexanediol mixtures in thin porous media using an Automatic Scanning Absorptometer (ASA). The limitations of this 1D model are discussed with respect to the nozzle dimensions and the liquid penetration depth. The penetration depth scales with liquid (viscosity and surface tension (η, σ)) and media parameters (average pore radius (r)) as predicted by Darcy’s law for Al₂O₃ disks that are inert to the liquid components. The penetration dynamics in PVDF and MCE filter membranes show a deviation from Darcy’s law, indicating specific liquid – media interaction with at least one of the liquid components. Furthermore a linear time regime is observed in the early stages of liquid penetration for time scales much larger than for which inertia effects are expected. This can on the one hand indicate that either, the liquid does not move into the fibrous samples as a homogenous liquid, or that the porous material deforms during the liquid imbibition process. On the other hand, it could be an effect resulting from the complexity of the porous structure itself and an indication of surface film flow formation.

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1. Introduction

Liquid transport in porous media is a very interesting, but generally also very complex physical phenomenon, which has a large range of possible applications in everyday life. On the other hand, understanding liquid transport in porous media enables one to positively influence the performance of a wide variety of applications, such as inkjet printing (Lundberg, 2011; Lundberg et al., 2006; Svanholm, 2007; Yang, 2003), heat storage (Nagel et al., 2013) or even diapers (Buchholz et al., 2005). On the other hand, knowledge of liquid transport in porous media can be vital to prevent damage as a result of salt intrusion in building materials (Pel et al., 2003). These are just some of the many examples where liquid transport plays a crucial role. To increase the effectiveness further, lower the costs or decrease the damage caused by liquid transport in porous media, a more profound understanding of liquid-media interaction during transport is necessary.

In general, liquid flow in porous media can be described by Darcy’s law (Darcy, 1856), where the nature of the pressure term driving the flow can either be external (permeability of a saturated medium) or internal in respect to the capillary pressure (absorptive flow through a saturated medium behind the wetting front). Over the years, extensions to Darcy’s law are made for deforming porous media (Anderson, 2005), unsteady flows (Khalifa et al., 2002), gravitational flows and multiphase liquid penetration (Muccino et al., 2010). Furthermore, the application of Darcy’s law in different liquid – media combinations has been...
addressed (O’Loughlin et al., 2013; Cao et al., 2015; Ridgway and Schoelkopf, 2011; Gruener and Huber, 2011). In order to test and validate Darcy’s law and to verify which extensions need to be taken into account for a specific liquid – media system, there is a need for experimental methods to accurately quantify the liquid transport in porous media in a time and space resolved manner.

This is especially true in the area of inkjet printing, where experimental data are limited due to the complex nature of the porous medium (paper) and the complexity of the used printing inks (Jaganathan et al., 2009). An important aspect of liquid absorption after jetting is that it occurs on short time and length scales, which limits the amount of experimental methods able to monitor liquid absorption real-time. Several experimental techniques have been applied over the years to study liquid penetration in paper. The oldest and easiest method is to section the studied samples after a certain absorption time and use gravimetric analysis. However this requires the use of several samples and can be very time consuming to extract the dynamic behaviour (Jaganathan et al., 2009; Ruoff et al., 1960) and results in a relatively low spatial resolution.

Methods that measure the liquid absorption by capillarity into porous media in situ range from gravimetric analysis (Liu et al., 2014; Schoelkopf et al., 2002) and high speed camera measurements (Lundberg et al., 2006; Koivula et al., 2012), to confocal microscopy (Li and He, 2011), neutron imaging (Gruener et al., 2011), infrared spectroscopy (Täg et al., 2010), UV–VIS spectroscopy (Lamminniemi et al., 2011), nuclear magnetic resonance imaging (De Azevedo et al., 2008; Kuijpers et al., 2017), electrical impedance spectroscopy (EIS) and automated scanning absorptometer (ASA) (Xu and Enomae, 2014; Lee et al., 2005; Suvarnakich et al., 2008).

The advantage of high speed camera measurements is the large range of timescales that can be addressed. However, the observed liquid transport is limited to the penetration dynamics in the field of view. Apart from transparent porous media, this is limited to the surface of the porous sample. Confocal microscopy can be used to measure in depth in porous media, but generally requires a fluorescent dye to obtain a sufficiently high spatial resolution. Gravimetric analysis, infrared microscopy, UV–VIS, EIS and ASA can measure at very short time scales (milliseconds). However, these techniques provide indirect information on the penetration depth which is averaged over the porous media volume.

The timescales accessible in the different techniques range from milliseconds to hours depending on the used technique. This excludes measurement techniques such as NMR and CT for measurements of the penetration dynamics in thin porous media since the timescale in which the uptake process takes place is too short to be captured by these techniques. An overview of optical and electrical impedance techniques applied to paper describing the advantages and disadvantages of the different techniques is given by Tomozeiu (Tomozeiu, 2016).

A drawback of most of the methods to measure liquid inside a porous material is the limited combinations of liquids and porous substrates that can be studied. For high speed camera experiments, a transparent porous medium is required. EIS relies on a non-conducting porous medium and a conducting fluid to measure liquid penetration. Furthermore, as EIS is probing conductivities and capacitances, a direct translation into liquid penetration involves a number of non-trivial assumptions. On the other hand, ASA can be applied on any porous substrate using any liquid capable of penetrating in the porous material. ASA monitors the liquid volume that penetrates into the porous medium in a given time (Suvarnakich et al., 2008). However, as a result, ASA needs a model to extract the penetration depth from the measured transferred liquid volumes, involving assumptions about both the liquid distribution and the penetration directions relevant for the studied problem. In all reported studies a 1D flow problem is assumed, but not justified (Xu and Enomae, 2014; Lee et al., 2005; Suvarnakich et al., 2008).

The present study aims to use ASA to quantify the penetration depth of liquids in thin porous media during capillary suction and interpret the ASA results to explain penetration behaviour. Therefore we introduce a data analysis method based on Darcy’s law to determine the penetration depth from the transferred liquid volume measured by the ASA setup. A criterion will be derived that enables validation of the 1D flow assumption. Firstly, to study the influence of the length and timescale on the capillary absorption, we compare the penetration dynamics measured by ASA on well-defined Al2O3 samples with a thickness in the order of millimeters to results obtained with 1D NMR imaging on similar liquid – media systems on centimetre sized samples. Secondly, we use ASA to measure 2 types of porous membranes that have a fibrous structure as found in printing papers. The fibers are non-absorbing, which allows to study the effect of pore size on the penetration dynamics.

2. Theory

2.1. Liquid transport in porous media

To describe liquid flow through porous media, one of the most commonly used expressions is Darcy’s law (Darcy, 1856):

$$\dot{q} = -\frac{K}{\eta} (\nabla P + \rho g z) \text{[m/s]},$$

(1)

where $\dot{q}$ is the volume flux through a porous medium, $P$ [N/m²] the pressure, $\eta$ [Pa s] the viscosity, $\rho$ [kg/m³] the density and $g$ [m/s²] the gravitational constant. We assume (a) that the absorbing liquid is incompressible and (b) that the porous media can be divided into two zones: dry and fully saturated. Based on these assumptions it follows from mass conservation that

$$\nabla \cdot \dot{q} = \nabla^2 P = 0.$$  

(2)

Darcy’s law can be applied to any three-dimensional porous material as long as the investigated medium is larger than the “representative elementary volume” (REV), the porous material does not change during liquid imbition, and the liquid flow is laminar. The REV indicates the minimum size of the porous medium, where the media parameters can be considered homogenous. Since Darcy’s law is only applicable for laminar flows, the dimensionless Reynolds numbers $Re$ in this study have to be below 2300. The Reynolds number depends on the density $\rho$, velocity $\nu$ [m/s] and viscosity $\eta$ of the imbibing fluid, as well as on the characteristic length scale $\delta$ [m] of the porous material:

$$Re = \frac{\rho \nu \delta}{\eta} [-].$$

(3)

The relevant characteristic length scale in this study is the average pore radius $r$ [m] of the porous material. The highest Reynolds number encountered in this study occurs when liquid penetration is fastest, so for water sorption in large pore sizes in the beginning of capillary sorption. This is of the order $10^{-4}$, which ensures laminar flow and allows the use of Darcy’s law to describe the liquid penetration dynamics.

In this study, we will neglect the gravity term in Eq. (1), which is allowed for sufficiently small Bond $Bo$ numbers. The dimensionless Bond number is defined as the gravity force divided by the capillary force:

$$Bo = \frac{\rho g \delta^2}{\sigma} [-].$$

(4)
The highest Bond numbers in this study occur for low surface tension liquids (i.e. containing surfactants) penetrating into the largest pore size samples and are of the order $10^{-8}$, which ensures capillary forces dominate the gravity forces and gravity can therefore be neglected.

2.2. Capillary suction in 1-D

To further simplify the governing equations, we use Darcy’s law in one dimension to describe the penetration depth of the liquid in the porous medium and assume the pressure difference only depends on the capillary pressure given by the Young-Laplace equation:

$$P_c = \frac{2\sigma \cos(\theta)}{r} \ [\text{Pa}], \quad (5)$$

where $\theta$ is the contact angle. Under these conditions we can rewrite Eq. (1) as:

$$q = \frac{\phi d l}{d t} = \frac{2\sigma \cos(\theta)}{\eta r} \ [\text{m/s}], \quad (6)$$

where the porosity $\phi$ of the porous medium relates the pore volume to the total volume of the porous medium. To obtain an expression for the penetration depth $l$ [m] of a liquid imbibing into a porous medium, we integrate Eq. (6) to obtain:

$$l = \frac{4K \sigma \cos(\theta)}{\eta \phi r} t \ [\text{m}]. \quad (7)$$

This model is only valid under the condition that the liquid penetration is a 1D process.

2.3. Suction from a dye

In the ASA method, liquid is absorbed in porous media via a dye. Here the conditions are discussed under which the liquid penetration from the dye can be considered as a 1D process. The dye has a length $L$ [m] and width $W$ [m] that moves over the surface of the porous sample with a speed $U$ [m/s]. This situation is schematically given in Fig. 1. The dye is connected to a liquid reservoir, which keeps the entire absorption area $A$ [m$^2$], determined by the dye dimensions, filled with liquid at all times.

To validate the use of a one-dimensional model to describe the liquid penetration behaviour we have to compare the contributions of the liquid flow in the three directions to the total absorbed liquid volume. Therefore we take one step back and compare the pressure contributions in three directions for the pressure gradient. From the pressure field, Eq. (2), we know that

$$\nabla^2 P = \frac{\partial^2 P}{\partial x^2} + \frac{\partial^2 P}{\partial y^2} + \frac{\partial^2 P}{\partial z^2} = 0 \ [\text{Pa}], \quad (8)$$

where $x$ and $y$ are the in-plane directions and the $z$ is the depth direction into the porous material. We can use normalised coordinates using the dye dimensions (width $W$ and length $L$) and the liquid penetration depth $l$ [m], defined as $x = x/W$, $y = y/L$ and $z' = z/l$, to obtain:

$$\frac{1}{W^2} \frac{\partial^2 P}{\partial x^2} + \frac{1}{L^2} \frac{\partial^2 P}{\partial y^2} + \frac{\gamma}{W^2} \frac{\partial^2 P}{\partial z'^2} = 0 \ [\text{Pa/m}^2], \quad (9)$$

Since the only significant pressure in the system is the capillary pressure, the second derivative of the pressure in any direction is always of the order $P_c$ as defined in Eq. (5). We can rewrite Eq. (9) using two conditions defined as $\zeta \equiv \left(\frac{x}{l}\right)^2$ and $\psi \equiv \left(\frac{y}{l}\right)^2$:

$$\zeta \frac{\partial^2 P}{\partial x^2} + \psi \frac{\partial^2 P}{\partial y^2} + \frac{\gamma}{W^2} \frac{\partial^2 P}{\partial z'^2} = 0 \ [\text{Pa}], \quad (10)$$

From Eq. (10) it can be seen that the problem is 1D when $\psi < 1$ and $\zeta < 1$. The first condition only depends on the dimensions of the liquid bath and is fulfilled for rectangular dyes, where $W < L$. The second condition depends on the liquid and porous media parameters via the penetration depth $l$. We can rewrite this condition as:

$$\zeta = \frac{4K \sigma \cos(\theta)}{\eta \phi r W} t \ll 1 \ [-]. \quad (11)$$

This indicates that the 1D assumption is valid for relatively slow uptake processes (high viscosity and/or low permeability) at short times.

3. Materials and methods

3.1. Experimental setup ASA

The Automatic Scanning Absorptometer (ASA) is a spiral-scan Bristow device based on the original Bristow wheel. The Bristow wheel method measures the absorption as the length of a liquid track left behind by a given volume of liquid (Bristow, 1967). A liquid container passes over the measured surface at a constant speed resulting in a constant absorption time (contact time). The absorption time can be varied by altering the speed of rotation of the wheel containing the measurement sample. The ASA method uses a horizontal disk to position the measurement sample under the liquid container following a spiral pattern. Furthermore, the rotational speed of the horizontal disk can be altered during a measurement sequence, which allows several absorption times to be measured in a single experiment.

In this research, an ASA device from Kumagai Riki Kogyo is used (KM 500win). ASA is designed to accurately determine the liquid penetration into porous media on timescales of milliseconds to several seconds. Fig. 2 shows a photograph and a schematic illustration of the experimental setup.

The ASA consists of a turntable (sample stage), scanning head (including nozzle), two types of glass capillaries (inner diameter 1.04 and 3.03 mm), and a sensor that follows the movement of the meniscus. The scanning head (shown in Fig. 3), made of stainless steel (SUS 304), has a slit with dimensions $L_{\text{slit}} = 4.9$ mm and $W_{\text{slit}} = 1.0$ mm. The maximum nozzle dimensions are $L_{\text{max}} = 6.2$ mm and $W_{\text{max}} = 3.0$ mm. The nozzle rests on top of the porous material placed on a turntable.

The glass capillary is connected with the scanning head via flexible Teflon tubes (with inner diameter ID = 2.0 mm). Liquid flows continuously from the glass capillary to the tip of the scanning head via liquid paths 1 and 2 as shown in Fig. 2b. At the start of
each measurement, the measurement liquid is absorbed into the tubes of the ASA measurement system from a container by pulling up the syringe using liquid paths 3 and 4 as shown in Fig. 2b. The Teflon cocks can be rotated to control which liquid paths are accessible. The glass capillary contains water and the water section and the absorbing liquid section of the Teflon tubes in liquid path 2 are separated by a short section of empty Teflon. The part of the Teflon tubes containing the liquid under investigation are replaced for each new liquid. The movement of the meniscus following liquid transfer to the porous material is measured by an optical sensor, which detects the meniscus location. The volume of the transferred liquid (TLV) is calculated from the movement of the meniscus.

When a liquid gets in contact with the surface of a porous material, the liquid starts to penetrate this material. During an ASA measurement, liquid will be supplied from a scanning head, which moves along a spiral path as visualised in Fig. 4. The measurement starts in the centre of the spiral. The rotational speed of the turntable is kept constant over a certain part of the track (grey sections), where after it will accelerate to the next constant value (green dotted sections). There is a small acceleration section after each measurement point. The measurement sections are alternately given in light grey and dark grey to clarify the different measurement sections. When the entire measurement is finished the turntable decelerates to a standstill (red striped section). The ASA system only measures the transferred liquid volume (TLV) during the times the rotational liquid is constant and records the time that the nozzle has been in contact with the media during such a section, defined as the contact time \( t \) [s]. Note that the width of the measured spiral is equal to the nozzle length \( L \). The ASA setup can measure at time scales from 10 ms up to 10 s. Due to the limited volume of the liquid reservoir in our equipment, measurements in this research are limited to a maximum contact time of 2 s.

### 3.2. Nozzle dimension considerations

An important parameter for the penetration depth calculations is the contact area \( A \) [m\(^2\)] of the liquid with the porous substrate:

\[
l = \frac{TLV}{A \phi} \text{ [m]}, \tag{12}
\]

where \( \phi \) [-] is the porosity of the porous material and TLV [m\(^3\)] the transferred liquid volume. The contact area for each measurement is shown in Fig. 4 as the grey area, which depends on the length of the nozzle \( L \) and the nozzle trajectory during the spiral movement in that section. In the case that the liquid is non-wetting for the nozzle, one can use the slit length \( L_{slit} \) [m] to determine the area of the porous material through which liquid can be absorbed. However in the case of a liquid that perfectly wets the nozzle, the liquid will spread over the nozzle surface area much faster than the penetration into the porous material, which results in an area determined by the maximum length of the nozzle \( L_{max} \) [m] indicated in Fig. 3. For a partially wetting substrate the area used to calculate liquid penetration is in between those two limiting cases.

The nozzle dimensions influence the ASA measurement calculations in the determination of the contact time \( t \). The contact time can be calculated using:

\[
t = \frac{W}{2 \pi f_{\text{turntable}} r_c} = \frac{W}{2 \pi f_{\text{motor}} r_c} \times 30 \times 10^{-3} \text{ [s]}, \tag{13}
\]

where the turntable frequency can be calculated from the motor frequency from \( f_{\text{turntable}} = \frac{f_{\text{motor}}}{30 \times 10^{-3}} \text{ [Hz]} \). The motor frequency \( f_{\text{motor}} \) [Hz] is a constant in each section and a direct output of the ASA software. The average spiral radius for the liquid penetration segment under consideration is given by \( r_c \) [m]. Depending on the wetting conditions of the liquid on the nozzle, the width \( W \) [m] can be equal to the slit width \( W_{slit} \) [m] (for non-wetting liquids), the maximum width of the nozzle area \( W_{max} \) [m] (perfectly wetting liquids) or a value in between.
To determine the nozzle dimensions to be used in this research, we compare two ASA measurements of water absorption on a porous Al₂O₃ disk with two types of nozzles: C and F. One nozzle has dimensions as shown in Fig. 3 (nozzle C) and a second nozzle has the side areas around the slit reduced to only 0.1 mm in both directions (nozzle F). Results calculated using the slit dimensions are shown in Fig. 5a and data processes with the maximum nozzle dimensions is plotted in Fig. 5b.

We observe that the uptake dynamics of nozzle F hardly change with a different choice of the nozzle dimensions, i.e. slit dimensions or maximum nozzle dimensions. On the other hand, there is a clear impact for nozzle C due to the non-negligible surface area of the nozzle beyond the slit area. In Fig. 5a, where we have used the slit dimensions to calculate the contact time and the penetration area, the liquid absorption for nozzle C is higher than for nozzle F for the same contact times. On the other hand, if we use the maximum nozzle dimensions (Fig. 5b), we observe a lower liquid uptake compared to nozzle F at the same contact time. Since the liquid penetration dynamics should only depend on the liquid and porous media conditions, which are identical in the measurements.
with both nozzles, the two curves should align in the situation where the contributing portion of the edges are taken into account. To determine the area of the edges that contributes to the liquid penetration process via the surface area and the contact time, depending on $L$ and $W$ respectively, we have used the raw data to recalculate $TLV/A$ and $\sqrt{t}$ where we use a fit of the form

$$L = L_{slit} + x(L_{\text{max}} - L_{slit}) [\text{m}],$$  

$$W = W_{slit} + x(W_{\text{max}} - W_{slit}) [\text{m}],$$

where $x [-]$ is a value between 0 and 1 and represents the portion of the side areas that contains liquid and therefore contributes to the liquid uptake. We assume that the portion of the contributing side areas is equal in both directions. We determine the value of $x$ as the value where both nozzles result in the same liquid absorption for the same contact time. This implies that the penetration dynamics are independent of the nozzle used. We find that this alignment occurs for a side contribution of 0.36, so when 36% of the side areas contribute to the absorption surface and the contact time. This results in a nozzle length $L$ of 5.43 mm and a nozzle width $W$ of 1.72 mm. This is determined for water penetration on the porous $\text{Al}_2\text{O}_3$ disks. Since the contact angle of water-glycerol mixtures on $\text{Al}_2\text{O}_3$ is very similar for the used glycerol concentrations (Kuijpers et al., 2017), we will use these values in the remainder of this study as a first order correction to calculate the surface area and the contact time.

3.3. Samples and liquids

In this research, three kinds of porous media are used: porous $\text{Al}_2\text{O}_3$ disks and two kinds of polymeric filter membranes.

3.3.1. Porous $\text{Al}_2\text{O}_3$ disks

The $\text{Al}_2\text{O}_3$ disks (Fig. 6a) are 150 mm in diameter and 5 mm in height and manufactured by Innalox B.V., where the porosity and average pore size was determined by Mercury Intrusion Porosimetry (MIP) (AutoPore IV 9500, Micromeritics Instrument Corp.). The pore size distribution (Fig. 6b) is measured for the 3 disks used in this study on a sample of the top and the bottom side of each disk. Distributions of different samples show small fluctuations, which result in small deviations in the average pore diameter ($D_{\text{avg}}$) and the porosity ($\phi$). The average pore diameter is determined from the measured total intrusion volume and the pore are ($4V/A$) which assumes the porous medium can be modelled as cylindrical capillaries. An average pore diameter of 0.20 ± 0.03 μm and an average porosity of 28 ± 1% was found. The average pore diameter and the porosity of the used samples are given in Table 1 at the end of this section. Furthermore, the tortuosity of the samples was measured by NMR by using stimulated echo’s (Kuijpers et al., 2017).

3.3.2. Polymeric filter membranes

The second class of materials studied are polymeric filter membranes, which have a fibrous structure and a thickness comparable to commonly used printing paper. The membranes used in this study are Durapore and MF-Millipore filter membranes produced by Merck Millipore. Both having a well-defined pore size distribution, the first type of membrane is made of hydrophilic polyvinylidene fluoride (PVDF) and the second is made of mixed cellulose esters (MCE). The MCE membranes consist of mixtures of cellulose acetate and cellulose nitrate and contain the surfactant Triton XVI. SEM images of both membranes are given in Fig. 7.

For each membrane type we tested two different average pore sizes to investigate the influence of the average pore size on the uptake dynamics. We measured the pore size distribution and the porosity of all four membranes using MIP and measured the tortuosity of the samples using NMR. The average pore size, porosity and tortuosity of the different membrane types are given in Table 1.

3.3.3. Liquids

Ink is a complex mixture of several different components, each having its own function. The most important components in

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness $\bar{z}$ [mm]</th>
<th>Average pore radius $\bar{r}$ [nm]</th>
<th>Porosity $\phi$ [%]</th>
<th>Tortuosity $\tau$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>5.0 ± 0.1</td>
<td>100 ± 35</td>
<td>28 ± 1</td>
<td>1.7 ± 0.9</td>
</tr>
<tr>
<td>PVDF</td>
<td>0.107 ± 0.01</td>
<td>148 ± 44</td>
<td>61.7 ± 0.2</td>
<td>1.6 ± 0.7</td>
</tr>
<tr>
<td>PVDF</td>
<td>0.108 ± 0.01</td>
<td>218 ± 44</td>
<td>59.9 ± 0.2</td>
<td>1.3 ± 0.7</td>
</tr>
<tr>
<td>MCE</td>
<td>0.107 ± 0.01</td>
<td>71 ± 44</td>
<td>62.2 ± 0.2</td>
<td>1.3 ± 0.7</td>
</tr>
<tr>
<td>MCE</td>
<td>0.155 ± 0.01</td>
<td>194 ± 44</td>
<td>69.9 ± 0.2</td>
<td>1.3 ± 0.7</td>
</tr>
</tbody>
</table>

Fig. 6. Example of an $\text{Al}_2\text{O}_3$ disks used in the ASA experiments (a) and the pore size distribution of the $\text{Al}_2\text{O}_3$ disks determined by MIP measurements (b).

Table 1. Physical properties of the porous media used in this study. The errors in the different quantities are the estimated uncertainties of the measurement method.
3.4.1. Media conditioning

Media are preconditioned at $T = 23.0 \pm 1.0 \, ^\circ C$ and relative humidity $RH = 50 \pm 5\%$. In case of the membranes, single samples/sheets are conditioned for at least 20 min on a rack located in the climate room. The $Al_2O_3$ disks are reused for several measurements. To make sure that all absorbed liquid components are removed, the samples are heated in an oven to 600 °C before each measurement. The heating temperature is higher than the autoignition temperature of the organic components used in this study. After heating, disks are left to cool at room temperature. Then the disks are equilibrated to the climatic conditions of the climate room for at least 20 min.

3.4.2. ASA measurement

At the start of a measurement a meniscus is created at the bottom of the nozzle by pressing down the syringe and pushing the liquid out of the Teflon tube into the nozzle. This meniscus is kept as small as possible to keep the initial error in the data acquisition as small as possible, while ensuring a good contact between the nozzle and the porous material. The measurement is then started and the rotating table starts to rotate resulting in an ASA measurement spiral as visualised in Fig. 4. The amount of liquid absorbed in each segment, or the transferred liquid volume is recorded by the ASA setup and the exact dimensions of the spiral are known from the experimental settings. The penetration depth can then be calculated for each segment using Eq. (12).

3.4.3. Data processing

The nozzle follows an Archimedean spiral during the ASA measurement. We calculate the absorption area of each spiral section from the experimental settings, such as the inner and outer radius of the contributing nozzle dimension ($r_{in} \, [m]$ and $r_{out} \, [m]$ respectively) and the polar angular coordinate $\theta \, [rad]$. This gives an absorption area for each segment $i$ equal to

$$A_i = \frac{1}{2} L (r_{c,i,\text{end}} - r_{c,i,\text{begin}}) (\theta_{i,\text{end}} - \theta_{i,\text{begin}}) \, [m^2],$$

with $r_{c,i,\text{end}}$ the average radius of the spiral at the start and $r_{c,i,\text{end}}$ the average radius of the spiral at the end of the measurement section. The centre position of the nozzle is calculated from the inner and outer radius of the spiral at that point from

$$r_{c,i} = \frac{r_{in} + r_{out,i}}{2} \, [m].$$

The nozzle length $L$ is calculated from Eq. (14).

4. Results

To obtain a quantitative measurement of the penetration depth of a liquid in a porous medium, first the accessible time scales and the reproducibility are characterized. The second step is to validate the used 1D Darcy model to calculate the penetration depth from the transferred liquid volume for which we use well-defined porous $Al_2O_3$ disks. We compare the results to NMR results reported by Kuijpers et al. (2017) using a similar liquid – medium system. Finally, we aim to investigate the possibility to extend the results to fibrous porous media, such as printing paper, using polymeric filter membranes with a fibrous structure and a well-defined pore.

Table 2

<table>
<thead>
<tr>
<th>Mixture composition [wt%]</th>
<th>Viscosity $\eta$ [mPa s]</th>
<th>Surface tension $\sigma$ [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water:Glycerol:Hexanediol</td>
<td>$0.92 \pm 0.01$</td>
<td>$72.3 \pm 0.1$</td>
</tr>
<tr>
<td>100:0:0</td>
<td>$1.86 \pm 0.01$</td>
<td>$70.2 \pm 0.1$</td>
</tr>
<tr>
<td>50:50:0</td>
<td>$5.38 \pm 0.02$</td>
<td>$68.5 \pm 0.1$</td>
</tr>
<tr>
<td>30:70:0</td>
<td>$20.0 \pm 0.1$</td>
<td>$66.1 \pm 0.2$</td>
</tr>
<tr>
<td>10:90:0</td>
<td>$172.4 \pm 0.5$</td>
<td>$65.1 \pm 0.2$</td>
</tr>
<tr>
<td>90:0:10</td>
<td>$1.32 \pm 0.01$</td>
<td>$25.8 \pm 0.2$</td>
</tr>
<tr>
<td>50:40:10</td>
<td>$5.51 \pm 0.01$</td>
<td>$27.6 \pm 0.2$</td>
</tr>
</tbody>
</table>
size distribution. The media are reasonably considered homogeneous over the thickness of the membranes, which should still allow the use of Darcy’s law to predict the liquid penetration dynamics.

4.1. Quantitative results using ASA

First we investigate the accessible time and length scales and the reproducibility of the ASA method. In Fig. 8, results for three different media are shown. An uncoated printing paper, a porous Al₂O₃ disk and non-porous Teflon. As expected, there is no absorption measured on the Teflon plate. The printing paper and the Al₂O₃ plates do show liquid absorption. The absorption in the Al₂O₃ plate is much faster, which is apparent from Fig. 8 considering the higher liquid absorption for the same contact time as compared to Teflon and printing paper. In this time, the average water penetration into the different porous media can be calculated using Eq. (12) and ranges from 50 μm to 4.3 mm.

The reproducibility of the method is tested by measuring the absorption of water-glycerol mixtures in the Al₂O₃ plates. The absorption of 25 wt% and 50 wt% glycerol in water is measured at least three times on the same Al₂O₃ plate and the results are presented in Fig. 9. The bars in Fig. 9 indicate the standard deviation in the measurement series. The spread in the results equals 10%, which indicates a good reproducibility.

4.2. Validation of Darcy model with porous Al₂O₃ disks

The second step is to validate the 1D Darcy model to calculate the penetration depth from the transferred liquid volume. Firstly, the square root of time scaling and the scaling with liquid (σ, η) and media (r) parameters predicted by Darcy’s law (Eq. (7)) are verified. Secondly, the ASA results are compared to NMR measurements by Kuijpers et al. (2017) on a chemically identical material at larger length and time scales. The only difference between the two types of samples apart from the length scale is the porosity which equals 28% in the samples used in this study as compared to 23% for the samples used by Kuijpers et al.

We investigate the uptake dynamics of mixtures containing water, glycerol and hexanediol into Al₂O₃ disks with an average pore size of 0.2 μm. Using these mixtures, we can investigate the scaling with viscosity (η) and surface tension (σ). The addition of glycerol to the liquid mixtures increases the viscosity, which can be changed over two orders of magnitude. By adding hexanediol we can substantially decrease the surface tension of the penetrating liquid i.e. in the order of 60% reduction. The viscosity and surface tension of the used liquid mixtures are described in Section 3.3.3. Fig. 10 shows the ASA measurements of the water-glycerol-hexanediol mixtures. As expected from Darcy’s law the penetration depth (l = TLV/A₀) at a specific contact time decreases with increasing glycerol concentration and the resulting increase in viscosity. We also observe the decrease in penetration depth resulting from the addition of hexanediol and the corresponding decrease in surface tension.

As described in Section 2.3, the penetration depth calculated from the liquid transferred volume is only accurate, while the liquid penetration can be regarded as a 1D process. This can be validated with the criteria given in Eq. (11). For the water-glycerol-hexanediol mixtures in Fig. 10, we are well below the limit described for ζ = l²/W², for which the highest value is of the order
$10^{-2}$, found for the uptake of pure water. Therefore the liquid penetration may be described by a one-dimensional model, such as Darcy’s law.

To validate the scaling predicted by Darcy’s law with viscosity and surface tension and to test the expected $\sqrt{t}$ behaviour we plot the predicted penetration depth $l$ on a rescaled x-axis ($\sqrt{\sigma/\eta \sqrt{t}}$) in Fig. 11. At least three measurements where conducted for each liquid - media combination.

After rescaling with liquid parameters ($\sigma, \eta$) and $\sqrt{t}$, all absorption measurements collapse on a single master curve. This shows the liquid penetration of water-glycerol-hexane-diol mixtures in porous Al$_2$O$_3$ can indeed be described by Darcy’s law and we can use Darcy’s law to predict the penetration depth of such liquids in the considered thin porous media.

A similar parameter scaling on centimetre sized samples was found with NMR imaging measurements (cylinders with a diameter of 20 mm and a height of 50 mm) (Kuijpers et al., 2017). Fig. 12 shows a comparison of the ASA results on thin Al$_2$O$_3$ plates with these NMR results. The results are presented on a log–log scale due to the large difference of accessible time and length scales of the two methods. The penetration depth ($l = TLV/\phi A$) in the ASA method is equivalent to the liquid front position, as determined for the NMR measurements. Fig. 12 shows that the results of both methods align on the same master curve, which implies that the same physical processes occur at both time scales. Furthermore it indicates that the parameter scaling with the viscosity and the surface tension holds, as predicted by Darcy’s law (Eq. (7)) on both length scales.

A more quantitative comparison of the ASA and NMR data is done as follows. A linear fit is made through the data points of each liquid separately, for both techniques. Eq. (7) is rewritten to obtain an expression for the slope of these fits:

$$l/(\sqrt{\sigma/\eta \sqrt{t}}) = \sqrt{4\kappa \cos(\theta)/\phi \cos(\theta) r_s} [m].$$

(18)

While the porosity $\phi$ and average pore radius $r$ of the materials are known parameters, the permeability and contact angle are the unknowns. To quantitatively compare the results of the ASA method with the NMR results (Kuijpers et al., 2017), we calculate the factors $\kappa \cos(\theta)$ for the ASA measurements and compare those to the values reported by Kuijpers et al. The values of $\kappa \cos(\theta)$ for each liquid mixture are given in Fig. 13.

The permeability factor ($\kappa \cos(\theta)$) deduced from both measurement techniques is found to be similar within the spread of the measurements, although the ASA results seem to show higher values. The two methods are expected to produce similar results, since the Al$_2$O$_3$ samples are produced by the same manufacturer following the same procedure, which should result in the same permeability. The only difference is the size of the samples and the porosity. The porosity of the ASA samples is slightly higher (28%) than of the samples for the NMR measurements (23%) and the permeability is proportional to the porosity. However the difference is small and does not fully explain the difference. On the other hand, the difference between the two methods is similar to the spread in the measurement results. Since the contact angle for water – glycerol mixtures on Al$_2$O$_3$ is very similar (Kuijpers et al., 2017) the values for the permeability factor are expected to be constant for different glycerol concentrations.

Since the penetration depth calculated from the ASA measurements shows a quantitative alignment with the direct measurement of the penetration depth using NMR (Acquaroli et al., 2011), we conclude that the measurement procedure can be used to calculate the penetration depth of water-glycerol mixtures.
penetrating in Al₂O₃. To investigate a wider applicability to more complex porous media, liquid penetration in porous filter membranes is investigated.

4.3. Model applicability to fibrous porous media

To investigate ASA application for penetration depth measurements of liquids in fibrous porous media, we conducted ASA measurements on polymeric filter membranes. These membranes have a well-defined pore size distribution, a well-known porosity and tortuosity and a fibrous structure similar to printing paper (Fig. 7). These membranes are homogeneous and do not contain filler materials or local fibre treatments, such as typically found in paper. Therefore, the membranes can be used to study the application of Darcy’s law to fibrous materials on length scales relevant for printing processes. Once again, we used water-glycerol-hexanediol mixtures to test the scaling with liquid parameters. We used two batches of membranes, PVDF and MCE membranes to investigate the dependency on liquid – media interaction.

4.3.1. PVDF membranes

The uptake dynamics of water-glycerol and water-hexanediol mixtures in two types of PVDF membranes, with an average pore radius of 0.15 and 0.22 μm, are presented as a function of time in Fig. 14.

Firstly, Fig. 14 shows slower uptake dynamics with an increasing glycerol concentration, as expected from the increasing viscosity. Secondly, the same liquids penetrate faster in the bigger pore size. This is consistent with the predicted penetration depth (Eq. (7)), as the permeability scales with \( r^2 \) (Kuijpers et al., 2017).

It is stressed that the PVDF membranes used in this study have a thickness of 0.11 mm, which means that any penetration beyond this point is a result of lateral liquid penetration into the porous material. Interpretation of the data in terms of a 1D penetration model cannot be done above this value. The penetration dynamics up to this point are compared with the prediction by Darcy’s law using a scaling with the liquid and media parameters \( (\sigma r t/\eta) \) in Fig. 15a. The expected square root of time behaviour is checked in Fig. 15b.

Fig. 15a shows the predicted time scaling with pore size, surface tension and viscosity holds, as the water-glycerol results align on a single curve for both membrane types (0.15 and 0.22 μm average pore size). Furthermore, we observe a much higher liquid penetration speed for the water-hexanediol mixture. Since we did not observe this specific behaviour for the water-glycerol-hexanediol mixtures penetrating in porous Al₂O₃ (Fig. 11), this indicates a specific interaction between hexanediol and the PVDF membrane.

Two regimes are visible for the uptake dynamics of water-glycerol in the PVDF membranes. In the early stages of penetration \( (\sigma r t/\eta < 0.5) \), (indicated by the light blue area in Fig. 15) linear uptake dynamics are visible whereas at later times we observe square root of time behaviour (Fig. 15b). If we assume that the porous medium is filled behind the wetting front, this effect cannot be fully addressed to inertia, as the transition to a viscous regime occurs at a time \( \tau \) of the order of milliseconds, according to (Quéré, 1997):

\[
\tau = \frac{pr^2}{4\eta} [s].
\]  

(19)

Ben Jazia et al. observed a similar effect for the absorption of water–ethanol microdroplets in polystyrene microbeads assemblies. (Ben Jazia et al., 2013). They attributed the linear time regime to a precursor film formation by the evaporated ethanol, accelerating the spreading of the imbibition front. Although water and glycerol are not as volatile as ethanol and are not expected to evaporate as easily, it is possible that a thin liquid film is formed on the fibers of the PVDF membrane resulting in a similar effect. This film can
behave as plug flow on the pore surface which extends the intertial time scale far beyond the time predicted by Eq. (19). A second possibility might be that the PVDF membrane swells, which can also alter the penetration dynamics and cause the liquid behaviour to deviate from Darcy’s law. Thirdly, the extended linear regime could be a result from the complexity of the porous material itself as suggested by Liu et al. (2014) and Schoelkopf et al. (2002). A closer investigation on the interaction between water, glycerol and hexanediol with the PVDF membrane is necessary to verify these hypotheses.

4.3.2. MCE membranes

We have done a similar study using the same water-glycerol mixtures on MCE membranes. We plotted the penetration depth of two membranes (0.07 μm and 0.19 μm average pore radius) as a function of rescaled times (σrt/η and √(σrt/η)); once again, the 1D penetration model can only be applied as long as the penetration depth is smaller than the membrane thickness (0.11 and 0.16 mm respectively for the two membrane types). The results are plotted in Fig. 16, where data points showing a penetration depth larger than the membrane thickness are omitted.

The scaling with the pore size also holds for this class of membranes. However, we observe an increase of the penetration speed with increasing glycerol concentration that cannot be attributed to the effects of viscosity and surface tension alone. This indicates that either the contact angle of water-glycerol mixtures on MCE membranes decreases with increasing glycerol concentration, or that glycerol has a very specific interaction with the MCE membranes. It is possible that glycerol acts as a plasticiser for this class of membranes.

Furthermore, Fig. 16a shows a linear regime for the early stages of absorption although not as pronounced as observed for the PVDF membranes (Fig. 15). This linear regime is also visible in Fig. 16b as the visible offset in time of a straight line through the data points. This effect could also indicate a formation of a thin wetting film via evaporation at the advancing menisci, or a swelling behaviour of the porous material, resulting in liquid uptake that can no longer be described by Darcy’s law. The swelling behaviour could be caused by one of the liquid components plasticizing the membrane, which can result in a linear absorption if the liquid penetration is no longer limited by the viscous drag. A more detailed study on the interaction of water-glycerol mixtures with MCE membranes is necessary to address these discrepancies with Darcy’s law.

5. Conclusion

In this study, we have shown the applicability of ASA to quantitatively measure the penetration depth of water-glycerol-hexanediol mixtures in thin porous media. A 1D model, based on Darcy’s law, is proposed to extract the penetration depth from the transferred liquid volume. The limitations of this 1D model are discussed using two criteria based on the nozzle dimensions and the liquid penetration depth.

Furthermore we show that roughly 36% of the side area of the nozzle has to be taken into account in order to obtain an accurate description of the absorption area and the contact time.

The penetration depth obtained with ASA measurements on thin Al₂O₃ samples are compared to NMR measurements on centimetre sized samples by Kuijpers et al. (2017) and show a relatively good agreement with respect to the spread in the measurements. The scaling with liquid (η, σ) and media parameters (r) is found to agree with the predictions of Darcy’s law.

When ASA is used to measure the penetration depth of water-glycerol-hexanediol mixtures in porous filter membranes, a deviation of scaling from the surface energy viscosity ratio suggests that the flow mechanism is other than equilibrium capillary flow. This deviation occurs for the PVDF membranes when liquids containing hexanediol are used and for water-glycerol mixtures on MCE membranes.

Furthermore, we observe a linear liquid penetration regime at the early stages of penetration that is too long to result from inertia effects. This could indicate the formation of a precursor film in the fibrous porous media as suggested by Ben Jazia et al. or could be related to a swelling of the porous material during liquid uptake given that one of the ingredients is able to plasticise the membrane. However, a detailed study on the interaction of these membranes with water-glycerol-hexanediol mixtures is necessary to understand this behaviour more profoundly.

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