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Sorption of water-glycerol mixtures in porous Al₂O₃ studied with NMR imaging

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HIGHLIGHTS

- NMR imaging can be used to quantify liquid component transport in porous media.
- Imbibition of water-glycerol mixtures can be described by Darcy’s law.
- Parameter scaling predicted with Darcy’s law holds in sub-micrometer regime.
- No separation of water-glycerol mixtures occurs during uptake in porous Al₂O₃.

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ABSTRACT

The penetration of water-glycerol mixtures in porous Al₂O₃ is measured using NMR imaging to quantitatively describe the liquid penetration and possible front separation of liquids in non-transparent porous media. We have studied the dependency on viscosity over two orders of magnitude by changing the glycerol concentration and have investigated the effect of pore size in the micrometer and sub-micrometer regime. We show that the liquid dynamics can be accurately described by Darcy’s law for all investigated liquid – media combinations and show that the permeability scales with the pore radius squared as predicted by permeability models by Lucas-Washburn and Katz-Thompson. Furthermore we have used T₂ relaxation analysis to investigate the homogeneity of the imbibing mixture during uptake and have found that water-glycerol mixtures penetrate the porous Al₂O₃ samples as a single homogeneous liquid.

1. Introduction

Liquid or gas penetration in porous materials is one of the dominant working principle in many 21st century applications. It is used to help control the ever growing CO₂ concentrations in our atmosphere resulting from the growing CO₂ production of our modern society by storing CO₂ in porous aquifers underground. In the process of CO₂ segregation, both storing and transporting the gasses into the porous materials are important (Bachu, 2008; Michael et al., 2010, 2009; Szulczewski et al., 2009). A second example is the conservation of monuments and sculptures. National heritage can get damaged by salt intrusion into the building materials. To effectively conserve the monuments and sculptures, knowledge of the liquid penetration processes is crucial (Gupta et al., 2012; Gombia and Bortolotti, 2008). Another example on a much smaller scale is the use of paper sensors where liquid penetrates through a piece of paper to reach the measuring zones (Böhm et al., 2014; Elizalde et al., 2015). The transport of the liquid needs to be slow enough to allow for all the reactions to take place, but should also be fast enough to get rapid results. A similar trade off happens in the inkjet printing industry, where a fast absorption of the ink is necessary to allow a high throughput, but the process should also maintain a reasonable print quality (Daniel and Berg, 2006; Lundberg, 2011; Svanholm, 2007). Furthermore, current research on liquid penetration in porous materials is applied in the manufacturing of diapers to effectively use so-called super absorbers. These materials absorb and hold the liquids very fast, increasing the comfort of the users without the necessity to increase the size of the diapers (Buchholz et al., 2005; Takahashi et al., 1997). Most of these applications require the ongoing research on liquid and / or gas penetration in porous materials to keep up with the constant demand for cheaper, faster and environmentally better materials and products.

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Since the original description of Lucas-Washburn's equation and Darcy's law, a lot of research has been performed on the applicability of these equations for a wide series of liquid - porous media systems (Szekely et al., 1971; Shikhmurzaev and Sprittles, 2012; O'Loughlin et al., 2013). Fisher and Lark studied the minimum pore size for which a Lucas-Washburn formulation is applicable for water and cyclohexane (Fisher and Lark, 1979), and found a deviation of Lucas-Washburn's law for water flowing in very small capillaries (0.3 μm). Even smaller capillaries were studied by Huber et al. Huber et al. (2007), they tested the influence of viscosity and surface tension by monitoring the imbibition of water and hydrocarbons in nanoporous silica glass with a mean pore radius of 5 nm. They, however, reported good agreement with the $\sqrt{t}$ behaviour predicted by Lucas-Washburn. Imbibition dynamics of water, n-alkanes and silicon oil in similar glass with pore radius 3.4 and 4.9 nm was studied by Gruener and Huber (Gruener and Huber, 2011), who also give an estimate of the applicability of Lucas-Washburn's equation and Darcy's law based on dimensionless numbers. Furthermore the effect of dynamic contact angle, which is sometimes given as a reason for discrepancies between experiments and the imbibition dynamics predicted by Lucas-Washburn, is discussed in varies studies. O'Loughlin et al. concluded that the dynamic contact angle alone cannot provide a consistent explanation for scaling discrepancies with Lucas-Washburn’s law for aqueous glycerol mixtures (O'Loughlin et al., 2013). Yang et al. have found that dynamics of the contact angle can be neglected in their study with a number of ethanol–water mixtures imbibition in a porous material consisting of glass beads (Yang et al., 1988). On the other hand, Popescu et al. conducted a series of experiments with high-viscosity silicone oil and water to test different models for dynamic contact angles, and found the possibility to accurately describe capillary rise dynamics using these models (Popescu et al., 2008).

Most of the research on liquid penetration up to the 21st century was done by studying the penetration of a single liquid in a simple porous medium. For present day applications however, the situation is not as straightforward and generally concerns multicomponent mixtures penetrating a complex porous materials (Gane et al., 2004). In the case of CO₂ storage the porous material can consist of multiple layers having different pore sizes and different interactions with the penetrating liquids or gasses (Hayek et al., 2009; Roels et al., 2016). Moreover, the solid in some of the layers can be displaced due to the imbibing gasses (Szulczewski et al., 2009). Changing of the porous matrix also occurs in the case of paper. The swelling of the material needs to be taken into account since the pore space and the resistance of the material to imbibing fluids changes when the paper is wetted (Anderson, 2005; Ridgway and Gane, 2005). This may also influence the print quality in case of inkjet-printed images (Bosco et al., 2015).

Apart from the porous media complexity also the complexity of the imbibing fluids forms a challenge in such applications. For example an inkjet ink behaves different from a single liquid due to the number of different components in the mixture. The interaction of the different components with the porous matrix can change the ink composition during uptake. Some of the components penetrate into the porous material whereas other components get stuck at the outer surface (Daniel and Berg, 2006). As a first estimate of the behaviour of complex liquid penetration in porous media, the main constituents are usually investigated separately. The following logical step is then generally to investigate the imbibition of a binary mixture of the main constituents.

The effect of such binary mixtures on the sorption dynamics and the scaling parameters of Lucas-Washburn’s equation and Darcy’s law have recently been studied with water–ethanol (Cao et al., 2015; Tagawa et al., 1998; Ben Jazia et al., 2011, 2013; Oh et al., 2010) and water–glycerol mixtures (O’Loughlin et al., 2013; Yang et al., 2011). Water-ethanol is used to investigate the effect of the liquid surface tension and contact angle in a number of studies (Cao et al., 2015; Tagawa et al., 1998). The imbibition dynamics were found to deviate from the predicted behaviour from Darcy's law and Lucas-Washburn's equation due to prewetting of the porous media by the ethanol phase (Ben Jazia et al., 2011, 2013). On the other hand, a study on water-alcohol mixtures in nanometre sized channels studied by Oh et al. (2010) shows that although the scaling with viscosity and surface tension holds for different water–alcohol mixtures, the prefactor from Lucas-Washburn's equation is off by 10–30%. The main reason for deviations from the simple descriptions by Darcy and Lucas-Washburn in water-ethanol systems is the volatile ethanol phase. This gives a changing liquid composition during uptake, which opposes the assumption of Darcy and Lucas-Washburn of a homogeneous liquid penetrating into a porous material. It would therefore be interesting to see if Lucas-Washburn’s equation and Darcy’s law do hold in a case where the two components of a binary mixture are not volatile, such as water-glycerol.

Mixtures of water and glycerol are used to study the effect of channel width in the case of an open microchannel by Yang et al. (2011). They found a good agreement with a modified version of Lucas-Washburn’s equation for the different flow profile in the non-cylindrical channels. On a slightly larger scale, the sorption of water-glycerol is studied in glass capillaries by O’Loughlin et al. (2013), who do observe discrepancies between the experimental observations and the theoretical expectations from Lucas-Washburn’s equation, which they attribute to a possible preferential adsorption of the water at the glass walls or a formation in the precursor film. In both cases, the behaviour in a channel is studied and the effect of an interconnected porous material is not addressed. Furthermore these studies have been performed in highly idealised porous media, i.e. single channels and capillaries. To test the validity of Darcy’s law and Lucas-Washburn’s equation in such liquid media combinations, the imbibition of water-glycerol mixtures in interconnected porous media is measured experimentally in this study.

Over the years a variety of experimental methods has been used to study imbibition in different porous media. The easiest method is to measure the weight change of the sample during imbibition or by simply checking the volume of the liquid that passes through the porous material in time (Ben Jazia et al., 2013). The main disadvantage of this method is that it gives an average over the entire porous material. For specific porous media such as glass capillaries (Quéré, 1997; Washburn, 1921), columns of glass beads (Yang et al., 1988; Davarzani and Marcoux, 2010) and sintered micro-models (Stevar and Vorobev, 2013; Courbin et al., 2009) the wetting front can be studied by optical measurements (Yang et al., 1988; Horgue et al., 2013; Glass et al., 2010; Weibrod et al., 2009) which give space and time resolved information of the imbibition dynamics. In the case of a homogeneous binary mixture however we cannot detect whether the mixture remains homogeneous or one of the phases penetrates the porous material faster than the other, which would result in a front splitting.

Since most applications are not necessarily transparent, a technique that allows space and time-resolved information which is also applicable in non-transparent media is preferred. A possible technique is Nuclear Magnetic Resonance (NMR) imaging, a non-destructive technique that allows to measure liquids locally and selectively, the latter implies that there is a possibility to use relaxation analysis to distinguish between different liquids, enabling to detect if a front splitting occurs (Gombia and Bortolotti, 2008; Blührich, 2000; Bayer et al., 2010; Stapf et al., 1996). The features of this technique are demonstrated in studies of, for example, dam-
age in building materials (Pel et al., 2003; Gummerson et al., 1979) but also heat storage with salts (Donkers et al., 2015). In these studies, the possibility to measure both moisture content and ions with NMR is utilized.

We use NMR to answer the two main research questions of this study. First we test the applicability of Darcy’s law and Lucas-Washburn’s equation for water-glycerol mixtures in interconnected porous media. Secondly, we aim to check the occurrence of liquid front splitting of these non-volatile mixtures during imbibition.

In this experimental study we use NMR to investigate the penetration of a mixture of two miscible liquids, water and glycerol in porous Al₂O₃ samples with different pore sizes, and look at the influence of viscosity and other liquid properties on the imbibition dynamics. Furthermore we check the scaling of Darcy and Lucas-Washburn’s equations in porous media with pore sizes in the micrometer and sub-micrometer regime. Finally we utilise the possibilities of NMR to investigate the potential de-mixing of the liquids during imbibition in the porous material.

2. Theory

To describe liquid penetration into a porous material, liquid properties, media properties and liquid – media interaction have to be taken into account. To start with a simple description of liquid flow through a cylinder we can use the law of Hagen-Poiseuille as given in Eq. (1).

\[
Q = -\frac{\pi r^4}{8\eta} \frac{\Delta P}{s}.
\]  

(1)

this gives the volumetric flow rate Q [m³/s] of a liquid with a viscosity \( \eta \) [Pa·s] due to a pressure difference \( \Delta P = P_{in} - P_{out} \) [Pa] over a cylinder with pore radius \( r \) [m] and length \( l \) [m]. By using the Hagen-Poiseuille law, we assume laminar flow, meaning low Reynolds numbers. The Reynolds number depends on the density \( \rho \) [kg/m³], the fluid velocity \( v \) [m/s], the characteristic length of the system \( \delta \) [m] and the viscosity \( \eta \) [Pa·s]:

\[
Re = \frac{\rho v \delta}{\eta}.
\]  

(2)

The characteristic length scale is equal to the average pore radius \( r_c \). In the liquid – media systems used in this study, the highest Reynolds numbers encountered are of the order of 10⁻⁶, which means laminar flow and allows the use of Hagen-Poiseuille law.

In order to apply Hagen-Poiseuille law to a porous medium, we need to take into account all liquid pathways and interconnections. To simplify the problem we assume that the internal structure of the porous material is homogeneous and can be described by an average quantity known as the permeability \( k \) [m²] as introduced by Darcy (1856). The liquid flux \( q \) [m/s] through a porous medium due to a pressure difference is then described by the well-known Darcy’s law:

\[
q = -k \frac{\Delta P}{\eta} \frac{m}{s}.
\]  

(3)

In the special case of a porous medium consisting of parallel capillaries with an average pore diameter \( r \), we can calculate the liquid flux directly by applying the Hagen-Poiseuilles law for all capillaries in the porous block and comparing this expression to Darcy’s law to find an expression for the permeability for this special case \( k_c \):

\[
Q = -\frac{\eta}{A} \frac{\pi r^4 \Delta P}{8} = -k_c \frac{\Delta P}{\eta} \frac{m}{s}.
\]  

(4)

After rewriting Eq. (4) and introducing the porosity \( \phi \) [−], which gives the fraction of the porous material available for liquid flow, we find:

\[
k_c = \frac{n \xi r^4}{8A} = \frac{\phi^2}{3}.
\]  

(5)

To extend the description to anisotropic porous media and to take into account that the pores are not simple straight capillaries, we introduce the tortuosity \( \tau \) to correct for the anisotropy of the material and to correct for the change in path length that occurs in a porous medium as compared to a bundle of straight capillaries. This is schematically visualised in Fig. 1.

This means that the volumetric flow rate gets modified to include the tortuosity, and the penetration length \( l \) gets corrected with a factor \( \tau \) as well. As a result we find that the permeability of a system of curved pipes \( k_{cp} \) with a narrow pore size distribution can be approximated by Eq. (6):

\[
k_{cp} = \frac{\phi^2}{3\tau^2}.
\]  

(6)

which is identical to a crude approximation of the Kozeny-Carman equation for cylindrical pores given by Zhang et al. Zhang and Scherer (2012). An approximation to allow the permeability to only depend on measurable parameters and eliminating the Carman parameter \( c \), which accounts for the shape of the pores, and the specific surface area \( 2/m^2 \) of the original expression by Carman and Kozeny:

\[
k_a = \frac{\phi^3}{c(1 - \phi^2)S}.
\]  

(7)

Another model for the permeability has been suggested by Katz and Thompson (Katz and Thompson, 1986) who based their permeability factor on percolation theory, the scaling is identical to the curved pipes case, only the numerical constant differs by a factor 4:

\[
k_t = \frac{\phi^2}{4\tau^2}.
\]  

(8)

In the situation of uptake of liquid in the porous matrix, the pressure difference is a result of the capillary pressure, given by the Laplace pressure \( P_l \). The Laplace pressure depends on the surface tension \( \sigma [N/m] \) and the radii of the curved meniscus in two directions \( r_1 \) and \( r_2 \). In the case of cylindrical capillaries and negligible gravity \( R_1 = R_2 = r_c \), the Laplace pressure becomes:

\[
P_l = \frac{2\sigma}{r_c} = \frac{2\sigma \cos(\theta)}{r}.
\]  

(9)

The radius of curvature \( r_c \) is related to the pore radius with simple geometric considerations (Gruener and Huber, 2011). To ensure gravitational forces do not play a significant role in this system.

**Fig. 1.** Schematic visualisation of the front position in a bundle of capillaries and the effective path length in a ‘real’ porous media.
the dimensionless Bond number has to be small. It is defined as the capillary force divided by the gravitational force:

\[ B_0 = \frac{\rho g \delta^2}{\sigma}, \]  

(10)

the characteristic length scale \( \delta \) is once again equal to the pore radius. In this study, the highest Bond numbers encountered are of the order of \( 10^{-10} \), which ensures that \( B_0 \ll 1 \) is always satisfied and gravity effects can be neglected.

Combining Eqs. (4) and (9) gives a differential equation, which can be solved by separation of variables:

\[ q = \phi \frac{dl}{dt} = -\frac{k}{\eta} \frac{2 \sigma \cos(\theta)}{r l}. \]  

(11)

In order to solve the differential equation we have to define the boundary conditions. In our experiments, the sample is partly submerged as schematically drawn in Fig. 2.

Depending on the fraction of the submerged sample we have to take into account 2D effects due to the liquid penetrating from the sides into the porous sample. In this study we neglect these effects, which is allowed only if the outside surface of the submerged part is small as compared to the bottom surface of the sample, so for \( 2l_0 < d/2 \), where \( dm \) equals the sample diameter,

\[ \frac{A_{\text{side}}}{A_{\text{bottom}}} = \frac{2 \pi l_0}{(1/4) \pi d^2} = \frac{2 l_0}{d/2} < 1. \]  

(12)

This means the average absorbed liquid is equal to the penetration length times the porosity \( \phi \). Secondly, we assume the sample is homogeneous, resulting in a flat liquid front penetrating into the porous material once the liquid inside the porous material has reached the water level outside the porous sample. Finally we assume the submerged part of the sample still contributes to the friction of the penetrating liquid column.

Under these conditions we can solve Eq. (11) using integration by parts resulting in the following expression for the penetration length \( l(t) \):

\[ l^2 = \frac{4 k}{\eta \phi} \frac{r}{\sigma} t + C, \]  

(13)

where \( C \) is the integration constant, which can be determined by the initial condition. We start the experiment at \( t = t_0 \), where the water starts penetrating into the sample resulting in \( l = 0 \). We then find \( C = -\frac{4 k}{\eta \phi} \frac{r}{\sigma} t_0 \), which results in the following expression for \( l' \):

\[ l' = \sqrt{\frac{4 k}{\eta \phi} \frac{r}{\sigma} (t - t_0)}. \]  

(14)

Depending on the porous medium the approximations from Lucas-Washburn’s equation or from Katz and Thompson can be used to estimate the permeability factor in terms of known quantities.

3. Materials and methods

3.1. NMR and methods

3.1.1. Principles

NMR (Nuclear Magnetic Resonance) imaging is a non-destructive technique that allows the determination of local moisture content inside a porous material (Blümich, 2000). The NMR measurements in this study were performed using a home built 1D NMR scanner tuned to measure hydrogen profiles similar to Kopringa and Pel (Kopringa and Pel, 1994). A static magnetic field \( B_0[T] \) of 0.7 T is generated by a water-cooled iron cored electromagnet. The sort of nuclei that can be measured depends on the local magnetic field \( B[T] \) and the frequency \( f \) [Hz] used to excite the nucleus.

\[ f = \gamma B, \]  

(15)

the proportionality factor is the gyromagnetic ratio, that depends on the nucleus to probe (for \(^1\)H \( \gamma = 42.58 \text{ MHz/T} \)). In order to create a spatial resolved measurement technique, a position dependent modification to the static magnetic field is applied using a gradient \( G[T/m] \):

\[ f = \gamma (B_0 + G x), \]  

(16)

where the position of the sample with respect to the centre of the magnet is given by \( x[m] \). When a RF pulse with a frequency matching the frequency in the magnetic field is applied, the hydrogen atoms can be excited and measured using a pick-up coil. The measured signal \( S \) is proportional to the number of hydrogen atoms in the measurement volume and decreases over time due to spin–lattice relaxation \( (T_1) \) and spin–spin relaxation \( (T_2) \). \( T_2 \) depends on the molecular structure of the probed liquid and on the surroundings of the nuclei (for example pore size). For moisture in porous material \( T_2 \ll T_1 \), the measured signals proportionality is given by

\[ S \sim \rho \left(1 - \exp \left(-\frac{t}{T_1}\right)\right) \exp \left(-\frac{t}{T_2}\right). \]  

(17)

where \( \rho [\text{kg/m}^3] \) is the nuclei density, \( t_1[\text{s}] \) (repetition time), the time between subsequent pulse sequences and \( t_2[\text{s}] \) is the echo time. There are different pulse sequences that allow the determination of the \( T_1 \) (longitudinal relaxation time). The \( T_2 \) (transverse relaxation time) can be determined by a CPMG measurement (Carr and Purcell, 1954). The stimulated echo sequence is used to determine the diffusivity inside the porous samples (Tanner, 1970). Each pulse sequence starts with a 90° pulse with a pulse length \( p_{90} \). After this 90° pulse, a second pulse is applied that is either the same (90°) or a pulse with the same length but an increased power (180°). After the echo time \( t_1 \) we measure the signal in a window width \( w w \). The proportionality of this signal to the number of ions and the relaxation parameters is given in Eq. (17).
To measure the tortuosity of our samples we use the diffusivity \( D \) of water in the porous samples and compare it to the diffusivity of bulk water \( D_0 \). Inside a porous medium diffusion is restricted by the pore walls, therefore the diffusivity in the sample is always smaller than the bulk diffusivity. This decrease can be quantified by the tortuosity factor \( \tau \) which is defined as in Eq. (18)Wong, 1999.

\[
\frac{D_0}{D} \equiv \tau = \left( \frac{L}{t} \right)^2 = \tau^2
\]  

(18)

The diffusion can be measured using a spin echo sequence, where three 90 degree pulses are applied (Tanner, 1970). This sequence is schematically drawn in Fig. 3. After the second pulse the ‘primary echo’ is measured and after the third pulse the ‘stimulated echo’ is recorded. Both the stimulated echo and the primary echo decay due to diffusion, \( T_2 \) and \( T_1 \) effects. However, we can exclude the effects of \( T_2 \) by looking at the quotient of the stimulated and primary echo, as a function of the time between the second and third pulse \( \tau_2 \). This results in

\[
\ln \left( \frac{M_{se}}{M_{pr}} \right) = -\left[ \frac{1}{T_1} + (\gamma G)^2 D \tau_2 \right] d_s
\]

(19)

where \( M_{se} \) and \( M_{pr} \) are the signal from the stimulated and the primary echo respectively. \( \gamma \) is the gyromagnetic ratio of the nucleus, \( G \) the magnetic field gradient, \( \tau_2 \) the time between the pulse and the echo and \( d_s \) the difference between \( \tau_2 \) and \( \tau_1 \). After saturating the porous samples with demineralised water and measuring the primary and stimulated echo intensity as a function of \( \tau_2 \), \( D \) can be calculated. Furthermore, the echo intensities for bulk demineralised water should be measured to get \( D_0 \).

3.1.2. Experiment details

In our setup, we use a static magnetic field of 0.7 T and have a gradient \( G \) of maximum 0.45 T/m. As a result we can measure the hydrogen concentration as a function of position with a resolution of maximum 0.7 mm. For this study, however, we used a smaller gradient of 0.23 T/m resulting in a resolution of 1.4 mm. As a result, each measurement point is the average of a slice with thickness 1.4 mm. The resulting frequency for hydrogen in our setup is 29.415 MHz.

To measure at different positions we use a step motor to move the sample through the sensitive area of the NMR equipment. In our case the step motor can be moved in steps of 0.85 mm. Besides the sample that is measured the sample holder also contains a reference compartment and the liquid bath of the penetrating liquid.

A schematic drawing of the NMR setup and the sample holder is given in Fig. 4. The combination of the setup and the sample holder allows the measurement of cylindrical samples up to 20 mm in diameter and 70 mm in height.

The liquids are fed to the sample holder (Fig. 4) through flexible tubes with an inner diameter of 2.4 mm and a wall thickness of 0.8
mm by two peristaltic pumps (Lead Fluid BQ50s). One pump is used to feed the liquid flow to the sample holder at 5 rpm, whereas the second pump pumps liquid back to the reservoir at 30 rpm. Since the connection of the outflow tube is above the connection of the inflow tube as well as 2–4 mm above the bottom of the sample, this ensures a constant liquid level just above the bottom of the sample. The sample holder allows air to enter from the top to prevent the formation of a vacuum.

To measure a liquid profile, we move the sample holder through the setup in 25 steps of 3.4 mm. This results in a total measurement range of 85 mm including the sample with a length of 50 mm, the liquid bath and the reference compartment. At each position, we conduct a series of measurements and each data point is the average of these measurements. The number of measurements is given by $n_{\text{avg}}$. A Hahn pulse sequence is measured at each data point to measure the water content. Every 5th point we use a CPMG pulse sequence to investigate the relaxation behaviour. Each liquid profile of 25 points takes 11.5 min to measure. Subsequent measurements are conducted until the samples are saturated.

The instrument settings for the used pulse sequences can be found in Table 1.

### 3.2. Samples and liquids

#### 3.2.1. Al$_2$O$_3$ porous cylinders

In this research, we use porous Al$_2$O$_3$ samples with a diameter of 20 mm and a height of 50 mm. We used three different sample batches with an average pore diameter of 0.2 μm, 1.2 μm and 16 μm. A SEM picture of the used sintered Al$_2$O$_3$ samples are given in Fig. 5. A thin layer of gold was sputtered on the surface to prevent charge build-up during SEM imaging. The bright white spots in the SEM pictures are an artefact of the SEM equipment used. The porosity of the samples is also extracted from the MIP measurements. We found that the porosity of the smallest pore sized sample is substantially smaller then for the larger ones. The sample properties are given in Table 2. The tortuosity is determined by stimulated echo measurements of bulk water and a water saturated sample and comparing the diffusion coefficients using Eq. (18).

#### 3.2.2. Penetrating liquids

The liquids we used in this research were obtained by mixing glycerol (>99.0% pure) with demineralised water. The mixtures were prepared by weight using a lab scale (Mettler Toledo PG2002-S) with an accuracy of 0.01 g. Mixing of the components was done by a vortex mixer (VWR 444-1372) for at least one minute. The liquid properties as a function of glycerol concentration are given in Table 3. The density, viscosity and surface tension are taken from literature (Glycerine Producers Association, 1963). The contact angles are measured on a chemically identical substrate used to manufacture the porous cylinders. However, these samples were sintered at a higher temperature to obtain non-porous Al$_2$O$_3$. We used a DSA100 (drop shape analyser) to measure the contact angles on the surface of the Al$_2$O$_3$. The error estimate for the contact angle measurement equals the standard deviation of the measured contact angle for at least 3 droplets and 3 measurements per droplet.

### 3.3. Experimental procedure

We start our experiments by measuring the (moisture) profile of the dry sample in the sample holder before adding the liquid. For a dry sample we measure no signal and we only obtain a signal from the liquid in the reference compartment. This profile is used to ensure a proper positioning of the sample holder as well as a check for residual liquids in the sample.
Next, we feed the liquid to the sample compartment for about 2 min and start the measurement. During this time, the empty area below the sample is filled with liquid. Approximately 30 s to one minute after the start of the experiment, liquid can be seen to exit from the outflow tube, which means the liquid has reached the outflow tube level and will remain at a constant level from that point onwards. The outflow tube is located at 2–4 mm above the bottom of the sample as shown in Fig. 4. Therefore the liquid has reached the bottom of the sample and imbibition starts around the same time the measurement is started.

Then, we measure subsequent profiles until the sample is saturated. An example of a water uptake experiment in 0.2 μm porous Al₂O₃ is given in Fig. 7. The position and time of each measurement point are stored and can be used to visualise the moisture profiles. We applied a spline interpolation procedure to determine the signal intensity at every point in time for all the positions. The spline interpolation and the measurement points on 4 positions in the sample are given in Fig. 7b. Using this interpolation, we can plot a profile at a specific time even though not all points are measured in one instant but are measured subsequently by moving the sample through the setup. An interpolation error can occur from the measurement noise if the measured signal intensity is very low. The interpolation error occurs for example near the end of the Al₂O₃ sample before the liquid has reached this position, resulting in a negative signal intensity or a signal intensity much higher than expected. This effect is visible at the interpolated time curve for position 70.9 mm in Fig. 7b. However, this only affects areas with very low initial moisture content and does not affect the signal intensity once the liquid front has passed.

As a result of the used time interpolation procedure to approximate the signal intensity at any point, a sharp front passing the position at a certain time will result in a gradual increase of the signal between the two closest measurement points. These points are about 500 s apart. Therefore, signal can be attributed to locations which are in reality not yet reached by the front which results in a visibly more inclined front. This effect is largest for fast moving fronts, so for the earliest profiles. As mentioned earlier, time interpolation is necessary to obtain a profile at a single time. Finally, the signal intensity is measured at points which are 3.4 mm apart and as a result the minimum front width in the profiles equals 3.4 mm.

Table 2
Sample properties of the Al₂O₃ cylinders used in this study as determined by MIP (pore size and porosity) and NMR (tortuosity). Using these values the theoretical permeability is calculated with Eqs. (6) and (8).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average pore diameter (2r) [μm]</th>
<th>Porosity (φ) [%]</th>
<th>Tortuosity (τ) [-]</th>
<th>Permeability (k_p) [Darcy]</th>
<th>Permeability (k_K) [Darcy]</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 μm Al₂O₃</td>
<td>0.21</td>
<td>22.8</td>
<td>1.9</td>
<td>0.08 x 10⁻³</td>
<td>0.02 x 10⁻³</td>
<td>Innalox</td>
</tr>
<tr>
<td>1.2 μm Al₂O₃</td>
<td>1.17</td>
<td>35.9</td>
<td>1.9</td>
<td>4.5 x 10⁻³</td>
<td>1.1 x 10⁻³</td>
<td>Innovacera</td>
</tr>
<tr>
<td>16 μm Al₂O₃</td>
<td>16.2</td>
<td>39.5</td>
<td>1.7</td>
<td>1.1</td>
<td>0.27</td>
<td>Innovacera</td>
</tr>
</tbody>
</table>

Table 3
Physical properties of the water – glycerol mixtures used in this study.

<table>
<thead>
<tr>
<th>Glycerol concentration [wt%]</th>
<th>Density (ρ) [g/cm³]</th>
<th>Viscosity (η) [mPa s]</th>
<th>Surface Tension (σ) [mN/m]</th>
<th>Contact angle on Al₂O₃ (h₀) [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.998</td>
<td>1.005</td>
<td>71.68</td>
<td>75 ± 2</td>
</tr>
<tr>
<td>25</td>
<td>1.060</td>
<td>2.13</td>
<td>69.59</td>
<td>80 ± 3</td>
</tr>
<tr>
<td>40</td>
<td>1.099</td>
<td>3.72</td>
<td>69.14</td>
<td>93 ± 1</td>
</tr>
<tr>
<td>50</td>
<td>1.126</td>
<td>6.00</td>
<td>68.39</td>
<td>89 ± 2</td>
</tr>
<tr>
<td>70</td>
<td>1.181</td>
<td>22.5</td>
<td>66.45</td>
<td>86 ± 4</td>
</tr>
<tr>
<td>90</td>
<td>1.235</td>
<td>219</td>
<td>63.76</td>
<td>82 ± 7</td>
</tr>
<tr>
<td>100</td>
<td>1.261</td>
<td>1410</td>
<td>62.28</td>
<td>96 ± 5</td>
</tr>
</tbody>
</table>
In Fig. 7, a domain at the bottom of the Al₂O₃ sample, is visible where the measured signal is higher than for the rest of the sample in the saturated case. This is due to the liquid present in the sample holder next to the submerged part of the sample as indicated schematically in Fig. 2. The front position is defined by the position where the liquid level is about 70% of the saturated sample liquid level. The position and time of this point are calculated by interpolation of the nearest measured points.

After an experiment, we heat the samples to 873 K to remove all water and glycerol by evaporation and thermal, decomposition respectively. We then let the samples cool at room conditions before using them for another experiment. To validate if samples could be used after heating we have measured water uptake, water-glycerol uptake and again water uptake with the same sample using the heating procedure in between. Both water-uptake experiments showed similar results, which indicates that the glycerol is indeed removed from the samples using this heating procedure.

4. Results

4.1. Water uptake

We first performed a set of uptake experiments with water to check the \( \sqrt{t} \) behaviour predicted by theory and to verify that different samples from the same batch give similar results. We therefore took 8 samples and measured the capillary suction of demineralised water into these samples. The resulting front position as a function of \( \sqrt{t - t_0} \) is given in Fig. 8.

Fig. 8 shows that all samples show similar front behaviour. Before plotting Fig. 8, the value of \( t_0 \) is determined by a straight fit through the raw data points to determine the intersection with the y-axis. We have also investigated the saturation level of all samples (measured near the top of the sample) and found that this is similar for all samples and gives a moisture content of 18 ± 2%, which is in line with the measured porosity by MIP (Table 2). The fluctuations we find for the saturated sample level are of the same order as the fluctuations of the saturation level within a sample, which is visible in Fig. 7 by the variation in the signal intensity of the final profile over the length of the sample (excluding the submerged part). This means the samples are indeed reproducible and we can compare measurements with different liquids, when we use different samples from the same batch.

We find a linear dependence of the front position \( l' \) with \( \sqrt{t - t_0} \) (Fig. 8) suggesting the process can indeed be described by Eq. (14). The slope of the line depends on liquid parameters, the contact angle of the demineralised water on the Al₂O₃ sample and the tortuosity of the Al₂O₃. A linear fit of the data results in a slope of 0.95. With the known liquid and media parameters (Table 3), we can calculate the permeability, which in this case is equal to 1.9 ± 0.5 \times 10^{-17} m² or 0.019 ± 0.05 millidarcy (md). From direct calculation of the permeability using the approximations given in Eqs. (6) and (8) we find values of 0.08 ± 0.06 md and 0.02 ± 0.01 md for the curved pipes and Katz-Thompson approximations respectively. The error approximations are calculated using the estimates of the errors in the measured quantities (\( \phi, r, \tau \) and \( d \)) as well as an estimate of the error in the literature values due to temperature fluctuations (\( \eta \) and \( \sigma \)).

4.2. Water – Glycerol mixtures

In the previous section we showed that the theoretical prediction (Eq. (14)) can be used to give an estimate for the liquid sorption of a single liquid in a ‘real’ porous material, but we find an uptake behaviour that is faster (higher permeability) than predicted by the theory. To check the scaling predicted by this theory, we investigate the sorption behaviour of a mixture of demineralised water with glycerol. We have measured the sorption of 25 wt%, 40 wt% and 50 wt% glycerol in samples with an average pore radius of 0.1 \( \mu \)m. The measured liquid uptake profiles are given in Fig. 9. From these profiles we then determine the front
position as a function of time. The addition of glycerol changes the surface tension and, more pronounced, the viscosity of the imbibing solution (Table 3).

By rescaling with the viscosity and the surface tension the theory predicts a single curve for all glycerol concentrations (since the contact angle does not change significantly (Table 3)). The front position as a function of the rescaled time is given in Fig. 10. The saturation levels for all liquids are found to be the same within the measurement accuracy. The spread in the data points results from an uncertainty in determining the time $t_0$ at which the liquid has reached the bottom of the sample and imbibition has started. Finally, there is an uncertainty in determining the front position due to the measurement points being 3.4 mm apart and each measurement point being the average of a slice with a thickness of 1.4 mm.

After rescaling, the curves for different glycerol concentrations collapse on a single master curve. Since the other scaling parameters (apart from the contact angle) are media quantities and do not depend on the liquid used, this indicates the predicted dependency on surface tension and viscosity is correct.

The contact angle is relatively constant, but is very close to 90 degrees (Table 3). Therefore, if we would calculate the permeability directly from the slopes in Fig. 10 we would have very large fluctuations and errors due to the multiplication with $\cos(\theta)$. We therefore calculate the value for the pre-factor containing the permeability as well as the contact angle and check to see if this value is constant with different imbibing liquids. For each liquid several measurements were conducted on different samples of the same batch. The pre-factor is found to be $0.07 \pm 0.02$ mD for all studied glycerol concentrations. This factor does not change with glycerol concentration as expected since the permeability should only depend on the medium and not on the penetrating liquid and the contact angle was found to be relatively constant for the measured water-glycerol mixtures on Al$_2$O$_3$ (Table 3). The jump in liquid penetration speed for water sorption in very small capillaries...
(<0.3 μm) as reported by Fisher and Lark (1979) was not observed in this research where the scaling as predicted by Darcy’s law still holds for an average pore diameter of 0.2 μm.

4.3. Effect of average pore size

The effect of the average pore size on the imbibition of water – glycerol mixtures is studied with 2 more batches of Al₂O₃ with an average pore size of 1.2 μm and 16 μm. We measured the uptake of water – glycerol mixtures in each sample and plotted the front position versus rescaled time. The bigger pore sizes allow us to measure with higher glycerol concentrations since bigger pore sizes speed up the process as can be seen from Eq. (11), as well as giving information on the applicability of Darcy’s law in micrometer sized pores. The results of measurements with higher glycerol concentrations in the 1.2 μm and 16 μm porous Al₂O₃ samples are shown in Fig. 11.

Fig. 11a shows the adjusted pre-factor i.e. \( k \cos(\theta)/\phi r^2 \) as calculated from uptake experiments, as a function of different glycerol concentration in samples with three different average pore sizes. The adjustment of the permeability with the contact angle is to decrease fluctuations and errors due to the contact angle being very close to 90 degrees. The second adjustment i.e. dividing the permeability by the porosity times the pore radius squared, allows a comparison of the different pore sizes in one graph as the permeability in both Lucas-Washburn and Katz-Thompson scales with \( \phi r^2 \) (Eqs. (6) and (8) respectively).

After correcting for the pore size we find that the pre-factor of the different sample batches is very similar, within the accuracy of the measurement technique, which corresponds to the scaling expected from the permeability models of Lucas-Washburn and Katz-Thompson. The other dependent quantity (tortuosity) is relatively constant for all samples, whereas the pore radius changes over 2 orders of magnitude.

![Figure 11](image)

**Fig. 12.** T₂ relaxation time distribution of water-glycerol mixtures in 0.2 μm Al₂O₃ (a), the pore size dependency of the T₂ relaxation time distribution (b) and the T₂ relaxation time dependency on pore size and glycerol concentration.
In Fig. 11b, the saturation liquid levels \( S \) for the same sample – liquid combinations are given after correction with the reference level \( S_{ref} \) and the porosity. Obviously, the saturation level is not unity in all cases, indicating air entrapment for some media liquid combinations. The error bars indicate the standard deviation of the measured signal between several measurements of the same liquid media system.

Since we can scale all liquid and media systems in this study to an approximately constant value for the adjusted pre-factor \( (k \cos(\theta)/\phi r^2) \) we can conclude that the uptake behaviour of water–glycerol mixtures in porous \( \text{Al}_2\text{O}_3 \) can indeed be described by Darcy’s law and that the permeability scales with \( \phi r^2 \). However, due to very large contact angles and the fluctuations in the measurements as a result of several measurement techniques, the exact value for the permeability and the best applicable theoretical model could not be verified.

O’Loughlin et al. (2013) have reported discrepancies between the theoretical expectations and the experimental results for water–glycerol mixtures penetrating in a vertical glass capillary. This discrepancy was found to increase with increasing water content of the solution. In this research, we were able to scale the liquid sorption behaviour with liquid and media parameters and found that the scaling behaviour as predicted by Darcy’s law holds for all water–glycerol mixtures. We have not observed a trend related to the increase of the water content in the mixture other than predicted by Darcy’s law.

4.4. \( T_2 \) relaxation analysis

The previous results show that the uptake dynamics of water–glycerol mixtures in the considered porous \( \text{Al}_2\text{O}_3 \) samples can be described with Darcy’s law. As this law applies to homogeneous liquids only, we may assume the water–glycerol mixtures can be considered as such. This implies there is no splitting of the front during uptake. This opposes the front-splitting behaviour of water–ethanol mixtures which were observed by Cao et al. (2015) where the ethanol phase could evaporate and form a pre-wetting layer in the porous material due to the lower boiling temperature of ethanol.

To verify the absence of front-splitting during uptake, the \( T_2 \) relaxation times halfway in the sample are measured as a function of time. If there would be a significant splitting of the water and glycerol fronts, this can be observed in the \( T_2 \) relaxation analysis, since the relaxation time of a water–glycerol mixtures in a porous medium is dependent on the glycerol concentration (see Fig. 12a). Here we show the \( T_2 \) relaxation distribution of 0.2 \( \mu \text{m} \) porous \( \text{Al}_2\text{O}_3 \) saturated with water–glycerol concentrations ranging from pure water to pure glycerol. Fig. 12a shows that the relaxation time decreases with increasing glycerol concentration and shows that the signal decay is mono-exponential as shown by the single peak in the relaxation distribution. We find the same mono-exponential behaviour in larger pore sizes (Fig. 12b) and the relaxation time increases with increasing pore size. This is to be expected, since the surface to volume ratio is smaller in larger pore sizes resulting in a less restricted movement of the nuclei and thus larger relaxation times. The inverse of the \( T_2 \) relaxation time calculated from the mono-exponential decay of the signal intensity is given in Fig. 12c as a function of glycerol concentration in the imbibing mixture for all pore sizes used in this study. We see that the differences in relaxation time are significant and can be measured using our measurement equipment. This indicates that a splitting of the front is detectable based on the differences in \( T_2 \) relaxation times.

The \( T_2 \) relaxation time behaviour during uptake of water–glycerol mixtures ranging from pure water to 50 wt% glycerol in water sorption is studied in 0.2 \( \mu \text{m} \) porous \( \text{Al}_2\text{O}_3 \). In all cases, a mono-exponential decay is observed (Fig. 12a), from the moment the liquid enters the measurement domain roughly halfway the measured sample. The measured relaxation times during uptake are shown in Fig. 13. We have subtracted the time it takes the liquid to reach the measurement domain \( t_{\text{front}} \) and rescaled the time with the viscosity and surface tension to compare the behaviour of the passing liquid fronts for different water–glycerol concentrations.

We observe that the relaxation time increases as the pores are filled by the passing liquid (the highlighted area in Fig. 13), after which it stabilizes to the final relaxation time of the saturated sample. As already observed in Fig. 12c, the final relaxation time of the saturated sample depends on the glycerol concentration in the mixture. In the event of front splitting (i.e. water moves quicker than glycerol) we expect a jump in the relaxation time as the 2nd liquid phase passes the measurement domain. The dotted line in Fig. 13 serves as a guide for the eye.

We do not observe such jump or additional plateau that could indicate a splitting of the front and the change of the \( T_2 \) relaxation time looks similar for all water–glycerol mixtures after rescaling the measurement time with liquid parameters. Therefore there is no indication of a splitting of the liquid front, further supporting the use of Darcy’s law for this liquid media system.

5. Conclusion

In this study we have used NMR imaging to measure the penetration of water–glycerol mixtures in porous \( \text{Al}_2\text{O}_3 \). We have found that NMR can be used to study the penetration dynamics of water–glycerol mixtures and allows the investigation of front splitting in non-transparent media. Relaxation time analysis has shown that the mixtures used in this study penetrate into the porous media as one homogeneous liquid without a splitting of the liquid fronts. We have studied the uptake dynamics of liquids ranging from 0 up to 90 wt% glycerol in water in porous \( \text{Al}_2\text{O}_3 \) with an average pore size of 0.2 \( \mu \text{m} \), 1.2 \( \mu \text{m} \) and 16 \( \mu \text{m} \).

The liquid front behaviour can be rescaled with liquid and media parameters to obtain one master curve. Our main conclusion is that the uptake behaviour of water–glycerol mixtures in porous \( \text{Al}_2\text{O}_3 \) can indeed be described by Darcy’s law.

The scaling with liquid and media parameters holds over several orders of magnitude for both viscosity and pore size in the
micrometer and sub-micrometer domain. Furthermore, we have also shown that the permeability scales with the pore radius squared, which is also predicted by the permeability models of Lucas-Washburn and Katz-Thompson. These results agree with the findings of Huber et al. (2007).

The pre-factor, which is incorporated in the permeability could not be verified due to the large fluctuations and errors arising from the contact angle measurements at very high contact angles near 90 degrees. In order to accurately describe the pre-factor the dynamic contact angle should be taken into account rather than the stable one as measured in this research (Cao et al., 2015), however this information is not available for the non-transparent porous media used in this research.

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References


