Imbibition on a porous layer: dynamical and mechanical characterization

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Solvent penetration in porous layers was analyzed using dynamical and mechanical characterization. Spreading dynamics of a solvent drop in a porous substrate provided parameters of the porous medium such as permeability and porosity. These measurements are relevant for many porous systems, for example paintings or porous varnishes and resins. We present direct visualizations of the drop as well as of the wet zone during the imbibition process and we evidence three distinct regimes. Experiments performed with various porous systems and different solvents highlight a universal behavior. The mechanical properties during the imbibition process are deduced through indentation testing measurements. We show that solvent penetration is responsible for the appearance of a viscous component in the system. A characteristic time depending on the solvent and on the porous medium is then deduced. The system recovers its initial mechanical properties and no swelling nor cracking is observed contrary to the case of paintings. This result tends to prove that visco-plastic properties are required to observe swelling or cracking.

1 Introduction

The phenomenon of imbibition in porous media is widely encountered in industrial situations or in the domain of cultural heritage particularly when restauration operations are carried out to remove and to replace the varnish layer of a painting. Indeed, the most common treatment used by curators to remove varnish consists in using organic solvents applied to solubilize the old varnish and to remove it. Generally, when a solvent penetrates in a porous layer, it can cause swelling or inversely a decrease of volume after solvent evaporation, and consequently, it can induce additional stresses on the matter which lead to the formation of cracks. In addition, the solvent can modify the interactions between the components of the porous medium and consequently implies modifications of the mechanical properties of the porous layer.

To prevent these undesirable effects, one needs to study the dynamics of solvent penetration in a porous substrate and the potential modifications induced on the matter such as: dissolution, variations of the mechanical properties, modifications of interactions between various components of porous medium or changes in the stress field due to swelling for example.

The aim of the presented work is to explain the physical mechanisms that come into play in imbibition processes and to identify physical macroscopic parameters, as relevant parameters, to describe the imbibition process for various porous systems which could be paintings, varnish or resins.

To this end, we propose to study the imbibition process of three different solvents in porous model systems formed after controlled drying of colloidal dispersions. The use of model systems has been motivated by the intent to deal with a well known and controlled system. The problem of solvent imbibition process on a porous medium has been studied by various authors; the widely used geometry is the case of a liquid droplet deposited on a porous substrate. Different situations have been addressed: the case of a porous medium partly or entirely filled with liquid, the case of a drop whose size is small or comparable to the size of the porous layer. The wetting properties, the viscosity of the liquid or its volatility are the main wetting parameters considered. Each parameter will play a role on respectively the spreading of the drop, the viscous flow in the drop or/and the diffusion in the porous and the evaporation. Davis et al. and then Alleborn et al. used lubrication theory combined with Darcy’s law to model spreading and sorption of a two-dimensional drop on a dry or saturated porous substrate. They obtained numeric profiles of the drop and of the wet zone, during the imbibition process. Some authors have included dynamic contact angle and contact angle hysteresis in their model or some employed Brinkman’s equation to solve the flow in the porous medium. Nevertheless, there are very
few experimental visualizations, to our knowledge, of both the drop and the wet zone in the porous medium during the imbibition process.\textsuperscript{10,11} In the present work, we propose an experimental study of the imbibition process based on direct visualization of simultaneously spreading and sorption of a drop on a porous substrate. The experimental profiles validate the numerical results obtained by solving both the lubrication and Darcy’s equations in the work of Alleborn and Raszillier (2004). We performed experiments with three different solvents and two porous media and found a universal behavior for the imbibition dynamics. In addition, we can estimate permeability of the porous substrate in two directions: parallel and perpendicular to the flow. We then present then indentation measurements conducted on the porous substrate before and after imbibition process to measure the impact of solvent penetration on the mechanical properties of the porous layer. Finally, we estimate dissolution of the porous media due to imbibition process.

2 Imbibition dynamics

2.1 Material and methods

The porous media of interest in this work are obtained during the drying of aqueous dispersions of silica colloidal particles: Ludox SM-30 and HS-40 commercially available from Sigma-Aldrich. The radius of silica particle is noted \( a \) and the initial particle volume fraction is \( \phi_{p,0} \) (see Table 1). The pH value is in the range of 9–10 to ensure that a high negative charge density is born by the particles; the DLVO theory is expected to apply and the dispersions are used without previous treatment. A liquid layer is formed by depositing a controlled volume of dispersion in a non-porous substrate (glass Petri dish), then the layer is left to dry from the free surface. The relative humidity is kept constant, RH = 54 ± 2%, at room temperature. Solvent evaporation concentrates the dispersion until the formation of a porous layer of approximately constant thickness in the centre of the container. The volume of dispersion initially deposited is chosen to obtain a solid layer thickness of around 1 mm.

As drying proceeds, shrinkage is frustrated by adhesion with the substrate. It causes large tensile stresses which lead to the formation of cracks which divide the layer into polygonal adjacent fragments. These fragments have been characterized through neutron imaging techniques to deduce the porosity \( 1 - \phi_p \) of their structure, where \( \phi_p \) is the particle volume fraction.

The permeability \( k \) is deduced from the Kozeny-Carman law based on the size of the nanoparticles.\textsuperscript{12,13} The main properties of the porous structure are reported in Table 1. One should note that we have considered fragments with no cracks as the presence of cracks will enhance and modify solvent penetration.

Three kinds of solvents are imbibed into the porous layers: water, ethyl acetate and glycerol. The choice of water and ethyl acetate has been motivated given their ordinary use by curators. Glycerol is not used in restoration but is a limiting case for the model due to its high viscosity and non-volatility. We have reported the main properties of the different solvents at \( T = 20 \, ^\circ\text{C} \) in Table 2.

The experimental setup used to follow the dynamics of imbibition is presented in Fig. 1. A fragment of uniform thickness is selected. The thickness of a fragment is measured by successively focusing on the top (air-layer interface) and on the bottom (layer-substrate interface) of the deposited film in transmitted light. The accuracy of this method is to within 3 \( \mu \text{m} \). Horizontality is adjusted by 3 screws on the sample holder. The experimental set-up allows us to image a fragment and provides both side and top view using two cameras (Marlin F131B, Allied Vision Technologies). Acquisition frequency is 1.875 frame per second (fps) for glycerol imbibition dynamics, whereas for water and ethyl acetate, we used a fast-speed

| Table 1 | Main properties of silica dispersions (particle diameter 2\( a \)) and porous media. \( \phi_{p,0} \) is the initial particle volume fraction of the dispersions. The volume fraction of the voids in the porous media is denoted \( 1 - \phi_p \) with \( \phi_p \), the particle volume fraction. The values have been determined by neutron imaging. \( k \) is the permeability calculated from Kozeny-Carman law.\textsuperscript{12,13} Measurements uncertainties are averaged over three different samples |
|-----------------|-----------------|-----------------|-----------------|
| System          | Colloidal dispersion | Porous medium   |
|                 | \( 2a \) (nm) | \( \phi_{p,0} \) | \( 1 - \phi_p \) | \( k \) (m\(^2\)) |
| SM-30           | 10            | 0.15 ± 0.04     | 0.83 ± 0.02     | 2 \times 10^{-20} |
| HS-40           | 16            | 0.22 ± 0.01     | 0.31 ± 0.03     | 3.7 \times 10^{-20} |

| Table 2 | Main characteristics of the solvents used for imbibition processes at \( T = 20 \, ^\circ\text{C} \). \( M_W \) is the molecular weight; \( \rho \), the density; \( \gamma \), the surface tension and \( \eta \), the dynamic viscosity.\textsuperscript{14,15} |
|----------|-----------------|-----------------|-----------------|
| Solvent  | \( M_W \) (g mol\(^{-1}\)) | \( \rho \) (m\(^{3}\) m\(^{-1}\)) | \( \gamma \) (mN m\(^{-1}\)) | \( \eta \) (mPa s) |
| Water    | 18             | 1              | 72.8            | 1              |
| Ethyl acetate | 88.1        | 0.9            | 23.9            | 0.46           |
| Glycerol | 92             | 1.26           | 63              | 1499           |

Fig. 1 (a) Experimental set-up composed of a sample holder, two cameras which acquire transmitted images. (b) Successive images during the imbibition of a glycerol drop on a porous system formed by drying Ludox HS-40.
camera EoSens 6546 CF 25-290 (Mikrotron GmbH) with a 200 fps frequency. A drop of a given volume is then deposited with a micropipette (Fisherbrand). The drop characteristic size is smaller than the capillary length ensuring an initial spherical cap shape for the sessile drops. The imbibition process takes place during a low duration in comparison with the evaporation timescale $t_0$, less than $<1/100$ (see Table 3). Thus, the whole drop that is deposited is assumed to penetrate into the porous layer. The drop and the wet area in the porous medium are illuminated by transmitted light, simultaneously. The two main advantages of the setup are the following. Firstly, the wet region can be followed with time by imaging successive profiles (see images in Fig. 1). Secondly, the axisymmetry of the deposited sessile drop and the wet region are easily followed using the top-view camera. Hence, the quantification of the profiles of both the sessile drop and the imbibed region reveals the conservation of the volume of liquid all along the imbibition process. This important point allows us to determine the volume of the imbibed region at each time.

The main parameters involved during the drop imbibition are reported in Fig. 2: the drop radius $r_d$ (the maximum radius is $r_{d,\text{max}} = r_d(t_0)$, reached at time $t_0$), the drop contact angle $\theta$ (the initial contact angle is noted $\theta_0$), the vertical penetration depth $z_{\text{imb}}$ at the center of the drop. $h_d$ is the drop height at its center, and the initial drop height is $h_{d,o}$.

### 2.2 Dynamics of drop imbibition

The same scenario is observed for the three used solvents and both porous media: the imbibition process can be decomposed in three distinct stages. In the first stage, the drop spreads on the porous fragment; the drop radius increases whereas the contact angle decreases (images 1–3 in Fig. 3(a) for glycerol). In a second step, the surface area of the drop contact base is constant: the contact line is pinned by surface defects and the contact angle still decreases (see images from 3 to 4 in Fig. 3(a)). Simultaneously, the solvent starts penetrating in the porous. Both radii, respectively of the drop and of the wet area are the same. In the last stage, the drop is no more pinned and its radius decreases as well as its contact angle. The radius of the wet area remains constant and equal to the maximum value of the drop radius whereas the vertical penetration increases (see Fig. 3(a), images from 4 to 10). At the end of the process, there is no more solvent outside the porous and the wet area is axisymmetric.

The time variations of the dimensionless drop radius, $r_d/r_{d,\text{max}}$ and dimensionless contact angle, $\theta/\theta_0$, are plotted in Fig. 4 for different initial drop volumes. Note that time $t_0$ corresponds to the end of the spreading stage of the drop and is chosen as a time reference.

We observe a brutal change of the slope for the drop radius correlated with the contact angle. These curves attest of a good reproducibility of the process. The data for experiments on two porous and with three solvents have been scaled with the Darcy’s time, $t_{\text{Darcy}}$, defined as the time for the drop to penetrate in the porous medium, hence: $t_{\text{Darcy}} = h_d^2/\gamma L$, with $\gamma$ the viscosity of the solvent; $h_d(t_0)$, the height of the drop when the drop radius is maximum (at the end of the spreading stage $t_0$); $(1 - \phi_p)$ is the porosity of the medium; $\kappa$ is the permeability determined by neutron imaging (see values in Table 1) and $P_{\text{cap}}$ is the capillary pressure which is the pressure of liquid in the pores of the system. Here, we take $P_{\text{cap}} \sim \gamma/\kappa$ where $\gamma$ is the solvent superficial tension and $a$ the particle radius. For water with HS-40 and SM-30 porous media, we found $9.3 \times 10^6$ Pa $\leq P_{\text{cap}} \leq 1.5 \times 10^7$ Pa whereas for ethyl acetate: 0.08 $\mu$L. Scale bar: 1 mm.

### Table 3: Comparison of Darcy’s time, $t_{\text{Darcy}}$ as a function of solvents and of porous media HS-40 and SM-30. $V_E$ is the evaporation rate. The drying timescales $t_d$ is defined as: $t_d = L_{\text{avg}}/V_E$ where $L_{\text{avg}} = 100 \mu$m is a typical length for drop penetration in the porous media.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>HS-40</th>
<th>SM-30</th>
<th>$V_E$ (m s$^{-1}$)</th>
<th>$t_d$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>10</td>
<td>11</td>
<td>$5 \times 10^{-4}$</td>
<td>2000</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>13</td>
<td>15</td>
<td>$1 \times 10^{-3}$</td>
<td>1000</td>
</tr>
</tbody>
</table>
acetate with HS-40 and SM-30 porous media, $3 \times 10^6$ Pa $\leq P_{\text{cap}} \leq 5 \times 10^6$ Pa. Table 3 shows values of $t_{\text{Darcy}}$ for water and for ethyl acetate on HS-40 and SM-30 porous.

Note that for a kind of porous, Darcy’s time of ethyl acetate is bigger than those of water. A possible explanation can be capillary condensation in the pores. In fact, ethyl acetate evaporates faster than water and condensation of ethyl acetate vapour can take place in the void spaces. This can modify the wettability of the silica particle surface. Thus, ethyl acetate penetrates faster and easier in the porous media than water, leading to a bigger imbibition speed inside the porous media. The drying timescale $t_d$ is defined as the drop mean height divided by the solvent evaporation rate $V_e$, for constant relative humidity. This evaporation rate has been measured by the mass loss with time of a volume of 5 mL, in a Petri dish, at ambient temperature and with a relative humidity of 50%. A typical length for drop penetration is $L_{\text{imb}} = 100$ µm. Table 3 shows the evaporation rate for water and ethyl acetate and the corresponding drying timescales.

All the curves collapse into a universal imbibition curve when plotted with the scaling time $t/t_{\text{Darcy}}$. A deviation is observed for dimensionless times about 10; at that time, the drop is very small and the resolution of the corresponding images do not provide enough precisions on the drop profiles. We have plotted as well, the height of the wet area $z_{\text{imb}}$ scaled with the height of the initial drop $h_{d,0}$. Again a universal behavior is evidenced.

The porosity values of the different porous media were deduced from neutron imaging techniques. We used a cold neutron imaging spectrometer. It allows performing radiography and tomography with fields of view ranging from 20 to 100 mm using a CMOS ANDOR NEO camera. Radiography can be performed with a field of view of 200 x 400 mm$^2$ by using a FUJI image plate. The incident neutron beam has a diameter of 20 mm, with a wavelength between 2 and 30 Angstrom. The spatial resolution is between 100 and 130 micrometers. The neutron beam passes over the sample (a fragment of the porous medium, obtained by drying, with a uniform thickness over the whole fragment) and we measured the transmitted light on an image formed thanks to a scintillator and a camera. By dividing the transmitted light of a sample filled with water with the transmitted light of a dry sample, we obtained the thickness of the sample traversed by the neutron beam and we deduce, knowing the total thickness of the sample, its porosity.

Another key parameter of the porous medium is the permeability which can be deduced from two different ways: using the Kozeny–Carman law or by direct measurements. This last method is based on the dynamics of the imbibition front depicted by the spatiotemporal diagrams presented on Fig. 5. We have recorded with time the vertical and the horizontal dashed lines to produce spatiotemporal diagrams of respectively the vertical and the radial imbibition front in the porous medium. We deduce the temporal evolution of the wet area $z_{\text{imb}}$ and its radial spreading $r_{\text{imb}}$. At the beginning of the imbibition process, evolutions of the fronts are linear and then become proportional to $\sqrt{t}$ to finally saturate. This behavior is similar to the dynamic of the capillary rise$^{20}$ as the liquid penetration in the porous medium is due to a pressure gradient in the pores of the system, that is the capillary pressure. There are then three stages in the capillary rise dynamics which depend on the dominant physical mechanisms. The first stage is a regime dominated by the inertial forces, then the second regime is called the...
Washburn’s regime where inertial forces become negligible compared to the viscous ones. The evolution of the imbibition front in the case of a porous medium is then given by:21,22

$$z_{imb} = \sqrt{\frac{\gamma \cos(\theta_p) r_{eff}}{2 \eta T^2} t} \quad (1)$$

Table 4  Comparison of mean pore radius determined by Washburn’s law for vertical and radial imbibition dynamics of a drop inside 2 porous media and mean pore radius determined by neutron imaging

<table>
<thead>
<tr>
<th>Porous media</th>
<th>Porosity $\phi_p$</th>
<th>$\kappa_K$ (m$^2$)</th>
<th>$\kappa_{Bear}$ (m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ludox SM-30</td>
<td>0.33</td>
<td>$2.0 \times 10^{-20}$</td>
<td>$2.0 \times 10^{-20}$</td>
</tr>
<tr>
<td>Ludox HS-40</td>
<td>0.31</td>
<td>$3.7 \times 10^{-20}$</td>
<td>$4.6 \times 10^{-20}$</td>
</tr>
</tbody>
</table>

**Sessile drop imbibition**

<table>
<thead>
<tr>
<th>Porous media</th>
<th>$r_{eff}^{vert}$ (nm)</th>
<th>$\kappa_{vert}^{Bear}$ (m$^2$)</th>
<th>$r_{radial}^{vert}$ (nm)</th>
<th>$\kappa_{radial}^{Bear}$ (m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ludox SM-30</td>
<td>1.66</td>
<td>$2.7 \times 10^{-20}$</td>
<td>3.0</td>
<td>$8.0 \times 10^{-20}$</td>
</tr>
<tr>
<td>Ludox HS-40</td>
<td>1.80</td>
<td>$2.9 \times 10^{-20}$</td>
<td>4.0</td>
<td>$1.5 \times 10^{-19}$</td>
</tr>
</tbody>
</table>

$a$: particle radius composing the porous media, $\kappa_K$: Kozeny–Carman permeability, $\kappa_{Bear}$: Bear’s law permeability, $r_{eff}$: effective radius of the porous and $T$, the tortuosity. The tortuosity is deduced from the porosity values through the relation:23–25 $T = 1/\sqrt{1 - \phi_p}$ and the permeability expresses as: $\kappa = (1 - \phi_p)/247 r_{eff}^2$, which is given by Bear.26

3 Evolution of the mechanical properties before and after drop imbibition

The mechanical properties of a porous medium strongly depend on its moisture content. This section is devoted to compare
the elastic behavior of a porous medium before and after drop imbibition. In this way measurements using indentation testing (CSM Instrument Micro-Hardness Tester – Anton Paar) were investigated on HS-40 and SM-30 layers of 1 mm thick. A typical experiment consists in the measurement of an applied force, \( F \), using a spherical indenter (Rockwell indenter of radius \( R_{\text{indent}} = 200 \mu\text{m} \)) as a function of the penetration depth, \( p \), as shown in Fig. 6. The maximum penetration depth of the indenter is always smaller than the solvent penetration depth (\( \approx 500 \mu\text{m} \)), except at the end of solvent evaporation from the porous media.

Assuming the material purely elastic within the limits of small deformations, the elastic response is well fitted using the Hertz contact law over a range of indentation depth such as \( p < 1.2 \mu\text{m} \) (Fig. 6). Hence, according to the classical Hertzian model, the applied indentation force \( F \) is determined by:\(^{29}\)

\[
F = \frac{4\sqrt{R_{\text{indent}}}}{3} \frac{E}{1 - \nu^2} p^\frac{3}{2} \tag{2}
\]

with the Poisson ratio \( \nu = 0.2.^{30} \) Typical elastic behavior of a porous medium before drop imbibition is shown in Fig. 6. It has to be noted, the water moisture content in the porous layer is not zero since the humidity rate of the surroundings is finite. Within the first minutes following the drop deposition, measurements using indentation testing do not allow us to estimate elastic response. Once the drop is totally penetrated inside the layer, measurements are possible in the wet region. The load-displacement measurements are then characteristic of a low elastic modulus. Further measurements show recovery with time of the elastic behavior of the porous layer (Fig. 6). Fig. 6 reports the case of ethyl acetate imbibition into HS-40 porous layers. Similar behaviors are obtained with SM-30 porous layers and with water imbibition, the timescales involved being different. The elastic moduli which are deduced from load-displacement curves and eqn (2), are shown in Fig. 7. Using the poroelastic theory it has been shown that the drying stress linearly increases with time.\(^{31}\) However, this model stated a constant elastic modulus with time. The recovery with time of the elastic behavior can be pointed out by the following simple arguments. Consider \( X \) being the current moisture content of the porous medium after drop imbibition. \( E_0 \) is the elastic modulus of the medium without solvent content addition, the linearity between stress, \( \sigma \), applied to the porous medium and its strain, \( \varepsilon_0 \), writes: \( \sigma = E_0 \varepsilon_0 \) in the conditions of applicability of the Hooke’s law. We observe no swelling of the material when water penetrated into the porous media, however, there is an additional deformation \( \varepsilon(X) \) due to imbibition that we assumed to be proportional to the quantity of solvent which has penetrated in the porous medium. The degree of solvent saturation affects thus the elastic response of the porous medium and this results in larger strain, \( \varepsilon + \varepsilon(X) \), and specific elastic modulus, \( E(X) \), such as: \( \sigma = E(X)(\varepsilon_0 + \varepsilon(X)) \). The solvent molecules and silica structures are assumed to be incompressible. Consequently, the strain resulting from the moisture content can be written: \( \varepsilon(X) = \varepsilon_0 \gamma X \) where \( \gamma \) is the volume per solvent molecule. The evaporation rate of the solvent is assumed to be constant during the main solvent removal period and is defined as: \( V_E = -\frac{\gamma}{S_0} \frac{dX}{dt} \) where \( S_0 \) is the evaporation surface. Finally the experimental results can be fitted by the law:

\[
E(X)/E_0 = 1/(1 + x(1 - t/t_D)) \tag{3}
\]

where \( x \) is a coefficient of the influence of the moisture content on the elastic properties of the material.\(^{32} \) This highlights the effect of solvent evaporation in the timing recovery of the elastic behavior of a porous medium previously imbibed. In order to observe swelling and cracking as a result of solvent imbibition and solvent evaporation, visco-plastic properties seem to be required.\(^{32-34} \)
4 Conclusion

We investigated the imbibition dynamics of three different solvents on two porous media. These porous media were characterized previously by neutron imaging. We implemented a set-up which permitted us to (i) verify the axisymmetry of deposited drops from a top view; (ii) to follow the drop profiles and the liquid front profiles inside the porous media. We described the imbibition dynamics by quantifying the drop radius, the drop contact angle, and the vertical penetration depth at the centre of the drop. A relevant characteristic time for imbibition is determined to be Darcy’s timescale: a universal behavior for different solvents and porous media is shown. These dynamics are completed with mechanical properties of porous media, before and after imbibition. Particularly, viscoelasticity was measured by creep measurements and show different characteristic times for water and ethyl acetate. Moreover, the fitting of micro-indentation loading curves with the Hertz’s contact law permitted the determination of Young’s modulus of the porous media before and after drop imbibition. A recovery of mechanical properties was evidenced as solvent evaporated. This result tends to prove that visco-plastic properties are required to observe swelling or cracking.

Conflicts of interest

There are no conflicts to declare.

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