

Liquid Penetration into Porous Media

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Abstract

A review of the principles of liquid penetration into porous media is presented, with emphasis on penetration of small drops (e.g. inkjet drops) into thin porous media (e.g. paper). The discussion consists of two parts: first, criteria of penetration are introduced, then the kinetics of penetration is analyzed. It is shown that the criteria of penetration depend not only on the material wettability (in terms of the contact angle), but also on the size of the liquid drop and the thickness of the porous medium. The kinetics of penetration of a drop into paper is shown to be different than theoretically expected. This is explained in terms of redistribution of the liquid between the paper pores. In addition, a method for the characterization of porous media by the kinetics of liquid penetration is presented.

Introduction

Liquid penetration into porous media is an essential process for many printing operations, especially those related to paper. The structure of porous media such as paper is very complex; thus, understanding the penetration process is a major challenge from an experimental as well as a theoretical point of view. However, in order to optimally design a printing system, it is essential to understand the underlying mechanisms. It is customary to start building this understanding by studying the penetration into a straight cylindrical capillary. This simplistic model highlights important aspects, however some essential features are missed. The next step is to treat a porous medium as a uniform collection of connected pores. Such a uniform porous medium is characterized by its porosity and specific surface area, without reference to local geometrical details. As will be shown below, this model may also be insufficient, and eventually the distribution of pores and their local structure will have to be considered.

A special feature of printing on paper, especially of inkjet printing, is the limited sizes of the elements involved: a very small drop has to penetrate into a very thin porous medium. The unit by which "smallness" or "thinness" are measured is the typical pore size. As will be explained in the following, systems of limited size exhibit special behavior during the penetration process. Another important problem that requires fundamental understanding of the penetration process is the characterization of porous printing substrates. It will be shown below how a simple approach based on the kinetics of penetration can assist in the characterization of paper. Thus, the goal of this paper is to review equilibrium and kinetic aspects of penetration into capillaries and simple models of porous media. It will be demonstrated that comprehending the underlying mechanisms may help in understanding important practical phenomena.

Equilibrium Aspects of Penetration

The main equilibrium aspect of penetration into porous media that is related to printing processes is the criterion of penetration. It is well known[1] that a liquid spontaneously penetrates into a porous medium when the contact angle it makes with the solid material is less than 90^o. When the liquid contacts a capillary, for example, it must form the appropriate contact angle with the solid wall. This makes the liquid-vapor interface curved. However, a pressure difference must be maintained across a curved interface at equilibrium, according to the Young-Laplace equation.[1] Thus, in order to maintain this pressure difference the liquid has to move in such a way that the pressure at the liquid side of the liquid-vapor interface adjusts itself. For example, if the contact angle is less than 90^o, the liquid goes up in a vertical capillary. By doing so, the pressure at the liquid side of the liquid-vapor interface is lowered relative to the atmospheric pressure, and the motion stops when the pressure difference is just the one required for maintaining interfacial equilibrium. If the contact angle is higher than 90^o, the curvature is such that the liquid tends to avoid penetrating into the capillary. Thus, the classical penetration criterion simply states that penetration is possible for contact angles less than 90^o and impossible for contact angles higher than 90^o.

Contact angles in the vicinity of 90^o are important for printing. This is so, since too low contact angles lead to feathering, while too high contact angles prevent penetration. It turns out, that when a small drop (such as an inkjet drop) enters a capillary (that serves here as a simplistic model for paper) the penetration criterion is different from the one described above for a large liquid reservoir.[2] In such a system, there exists an additional driving force for penetration: the elevated pressure inside the small drop. This additional driving force, which depends on the drop radius, stems from the energy that was invested in creating the surface of the small drop. It may enable penetration at contact angles higher than 90°. Thus, the penetration criterion for small drops, especially for contact angles in the vicinity of 90°, depends on the size of the drop.

Another size-related aspect of penetration is the effect of the thinness of the porous medium. In general, a liquid penetrates into a capillary or a porous medium since it energetically prefers to be in contact with the solid surface rather than with the surrounding air. However, in a thin porous medium, the liquid that enters is re-exposed to air through the pores at the surface of the medium. Obviously, this aspect becomes more dominant as the porous medium becomes thinner. It turns out[3] that this "re-exposure effect" may lead to an unexpected equilibrium state, as shown in Fig. 1: the liquid may reach equilibrium when the radius of the base of the drop above the paper equals the radius of the wet stain inside the paper. This state is termed "basal penetration." The reason can be explained with the aid of Fig. 1. Before the liquid reaches basal penetration, the liquid in the drop above the paper is exposed to air inside the porous medium. Had the liquid penetrated beyond the basal penetration state, the liquid inside the porous medium would have been exposed to the outside air. Thus, liquid-air contact is minimized at the basal penetration state. This effect contrasts the expected behavior of complete penetration for contact angles smaller than 90°. It is, naturally, more pronounced for contact angles that are relatively close to 90°.

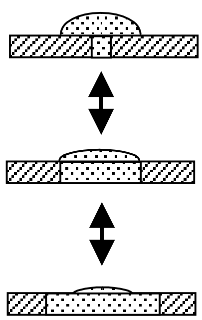

Figure 1. Basal penetration and related situations

Kinetic Aspects of Penetration

The fundamentals of the kinetics of penetration into a capillary were worked out many years ago by Lucas[4] and by Washburn.[5] One of the well-known results is the diffusion-like dependence of the penetration distance on time for a horizontal capillary:

$$x^2 = \frac{\sigma(r\cos\theta)}{2\mu}t \tag{1}$$

where x is the penetration distance, σ is the surface tension of the liquid, r is the radius of the capillary, θ is the contact angle, t is the time, and μ is the viscosity of the liquid. For a vertical capillary one gets

$$At = -Bh - \ln(1 - Bh) \tag{2}$$

where h is the penetration height, and

$$A \equiv \frac{\rho^2 g^2 r^3}{16\sigma\mu\cos\theta} \tag{3}$$

$$B \equiv \rho g r/(2\sigma\cos\theta) \tag{4}$$

where ρ is the density of the liquid and g is the gravitational acceleration.

Comparing Eqs. (1) and (2), it becomes clear that the effects of radius and contact angle on the kinetics of penetration are quite different in the two cases. For a horizontal capillary, the effects of r and θ cannot be separated by measuring the kinetics of penetration. This is so, since from x vs. t data one can deduce only the product $r\cos\theta$. On the other hand, for a vertical capillary, r and θ are not linked, and can be independently calculated from kinetic data. This observation enables the calculation of an effective radius and an effective contact angle as a simple and convenient tool for paper characterization.[6] The term "effective" implies a value that would lead to the same kinetics in a straight cylindrical capillary. Sample results calculated by this method for filter papers demonstrate that the effective contact angle turns out to be much higher than expected. This is so, since the effective contact angle calculated for a porous medium from Eq. (2) accounts also for the structure of the porous medium, in addition to the surface properties of the solid and liquid.

An important practical problem is the rate at which a drop penetrates into paper. According to a simple theoretical model of a radial capillary,[7] which is supposed to represent a uniform porous medium, the area of the wet stain should approximately be proportional to $t^{0.9}$. However, this prediction is not supported by experimental data. Careful experiments by Kissa[8] demonstrated that the area of the wet stain is approximately proportional to $t^{0.3}$. This major difference between theory and experiment was explained by performing some simple additional experiments,[9] as described in the following. Fig. 2 shows the simple setup that was used. Liquid from a small dish was fed into a filter paper by a short glass capillary that touched the paper. As long as the liquid was flowing into the paper from the dish, the kinetics of the expansion of the wet stain in the paper approximately followed the $t^{0.9}$ dependence, in agreement with the theoretical prediction. Once the feed was discontinued by disconnecting the small capillary, the $t^{0.3}$ dependence approximately prevailed. Thus, it is clear that the kinetics depends on the size of the liquid reservoir. When there is only a finite amount of liquid, as in the case of a small drop, the kinetics is much slower. This is explained by a mechanism that depends on the nonuniform structure of the paper. The reason for the expansion of the wet stain when the amount of liquid is finite is transfer of liquid from the large pores into the small ones (that have a higher driving force for capillary penetration because of the smaller effective radius).

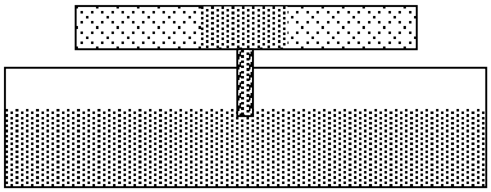

Figure 2. Setup for studying liquid penetration rate into paper

Conclusion

It has been demonstrated that the process of capillary penetration in printing operations may depend on complex and subtle effects. These include the complex geometry of the pores in paper, the thinness of paper and the smallness of ink drops in inkjet printing.

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Biography

Prof. Abraham Marmur has been working in the field of interfacial phenomena and wetting for over twenty five years. He has published many papers on the theory and practice of wetting processes, and has been consulting for major companies involved in the design and utilization of inkjet printing systems. He was also an editor of Reviews in Chemical Engineering, and was on the advisory committee of J. of Colloid and Interface Science and J. of Adhesion Science and Technology.