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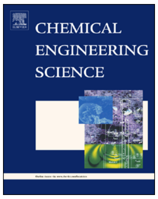

Coffee stains on paper

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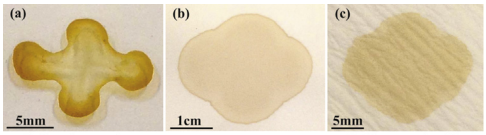
HIGHLIGHTS

- The first mechanistic study that clarifies coffee ring phenomenon on paper.
- Examples and analysis of ring-like and non-ring-like stains on paper.
- Insights into controlling shapes of coffee stains for paper-based sensor design.
- Implications of transport behaviour of dispersed material in porous media.

GRAPHICAL ABSTRACT



Coffee ring on glass **Coffee ring on paper** **Coffee non-ring-like stain on paper**

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ABSTRACT

In this study we investigated the underlying mechanisms of coffee stain formation on paper – a porous substrate. When a drop of aqueous liquid containing dispersed materials dries on paper, the faster water evaporation rate at the edge of the drop drives the redistribution of the dispersed materials to the edge of the drop-covered area on paper. Deegan's discovery has been accepted as the “coffee ring” phenomenon, which has wide implications. However, stains left by dried aqueous liquids on paper are not always ring-shaped. This is because, besides Deegan's coffee ring effect, the transport of dispersed materials in porous media is affected by chromatographic and filtration effects, which are highly dependent upon the properties of the substrates. In this work we clarify the influences of different mechanisms to the dispersed materials redistribution in paper.

1. Introduction

When coffee is spilt on paper and stains the paper, a coffee ring may or may not form at the edge of the spill. Despite that paper has been used to demonstrate the coffee ring phenomenon (Spiegel, 2014), the formation of ring-shaped coffee stain on paper can be caused by mechanisms different from the “coffee ring” phenomenon first reported by Deegan et al. (1997), and later elucidated by many others (Bhardwaj et al., 2010; Eral et al., 2011; Hu and Larson, 2006; Weon and Je, 2010; Yunker et al., 2011). Deegan et al. studied the coffee ring phenomenon on non-porous solid surfaces and showed that the formation of a ring-shaped deposit of dispersed materials in the liquid is driven by the radial and outward flow of the liquid during drop drying. The higher evaporation flux at the pinned edge of a drop forces the liquid to flow from the centre of the drop towards the edge to replenish the faster liquid loss at the edge. Consequently, a ring is formed because of the pinning and enhanced evaporation at the wetting line. Deegan et al. showed that the coffee ring phenomenon is independent of the substrate or the liquid system that carries dye or suspended colloids. This phenomenon influences processes such as printing, washing and coating (Deegan et al., 1997). Further understanding of the coffee ring phenomenon was made by Hu et al.; these researchers showed that the suppression of Marangoni flow inside an evaporating drop is another necessary factor to ensure the formation of the coffee ring (Hu and Larson, 2006). More recently Dou and Derby (2012) studied drying of small ink jet ink drops on porous particles beds and showed that patterns of coffee stains could be influenced by the pore size of the powder bed. They proposed that drainage flux (liquid phase enters the porous bed by capillary absorption) and the evaporation flux simultaneously influence the pattern of coffee stain.

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Unlike the above mentioned coffee ring phenomenon (Deegan et al., 1997; Hu and Larson, 2006; Dou and Derby, 2012), the stain patterns left by dried liquid drop on paper may or may not be ring-shaped. The fundamental reason is that paper is a porous substrate and the transport of the dispersed materials with liquid in paper is affected not only by faster liquid evaporation rate at the wetting front, but also by chromatographic and filtration effects. These effects are dependent on the properties of the paper, the liquid and the affinity of the dispersed materials with fibres in paper.

The forming mechanisms of coffee stain on paper are relevant to industrial processes involving interactions between porous materials and liquids containing dispersed materials, such as printing, chromatographic separation and filtration. Coffee stain on paper is also relevant to paper-based microfluidic and diagnostic devices. An assay is usually performed by introducing a small quantity of sample onto a paper sheet or into certain patterned areas of a paper-based microfluidic devices, the final distribution of the indicator colour on paper microfluidic devices can significantly affect the outcome of the colour evaluation (Li et al., 2010a). Although the coffee ring has been largely ignored in many paper microfluidic studies (Carrilho et al., 2009; Chitnis et al., 2011; Chung et al., 2012; Dungchai et al., 2010, 2011; Lewis et al., 2012; Li et al., 2010b, 2010c; Martinez et al., 2010a, 2008, 2010b; Mentele et al., 2012), there have been a small number of studies investigated on how to suppress coffee ring on paper devices (Määttänen et al., 2011). Here we present a preliminary study on patterns of coffee stains on paper to clarify their differences from coffee rings on non-porous substrate, and to reveal the mechanisms responsible for the formation of stains on paper. This understanding will be useful for the control of material transport in paper and in porous substrates in general.

1.1. Theoretical background of water transport and absorption in paper

Water transport in and absorption by paper is determined by two processes: capillary penetration through the inter-fibre gaps (Stock and Rice, 1974), and liquid absorption by cellulose fibre wall (Bristow and Kolseth, 1986; Li et al., 2010a). Bristow and Kolseth (1986) showed that for aqueous solutions capillary penetration through the inter-fibre gaps into fibre network is the dominant mode of water transport in paper (Fig. 1). Although water absorption via the fibre wall occurs at the same time, it is a slower process compared with the capillary penetration. For hydrophobic paper, i.e., paper treated with hydrophobization reagents, the wettability is reduced and the apparent contact angle between the water and paper surface increases (Shen et al., 2000). When the apparent contact angle is significantly greater than 90°, water transport through the fibre network stops; water transport by paper can only occur via the fibre wall absorption. This process is slower than water evaporation and therefore a water drop can remain on hydrophobic paper until it evaporates completely. Bristow et al. described these liquid transport processes using a schematic diagram and experimental data (Fig. 1) (Bristow and Kolseth, 1986).

2. Materials and methods

Whatman (1, 597 and 113) filter papers (Sigma-Aldrich) were selected as standard porous substrates. Fluorescent yellow-green carboxylate microspheres (4.5 μm, 2.6%, Bio-Scientific) were diluted 10,000 times with distilled water. Aqueous commercial food dye solution, containing food dye 133 (brilliant blue FCF) was diluted 10 times with distilled water. Coffee (Decaf, Nescafe) was dissolved in distilled water to prepare a concentration of 20 mg/mL for use. Paraffin wax (55 FRG, Dussek Campbell, Australia) and alkyl ketene dimer (AKD, Konz 88, BASF)-heptane solution of 0.6% w/v (8, 15) were used for paper hydrophobization. Images were captured by the digital camera (Apple iPhone 5, auto colour photo setting without flash light; object distance of 10 cm). UV light (254 nm) and Nikon Ai1Rsi confocal microscope were used to capture images of fluorescent beads in paper.

The water drop evaporation rates were measured by the mass loss rate of a drop of 6 μL of distilled water was deposited on AKD treated Whatman 1 filter paper and a wax treated glass slide, respectively.

A dye stain pattern experiment was performed on a Whatman 1 filter paper placed inside a Petri dish which was tightly covered by a paraffin film. A small hole was punched in the middle of the film with a syringe. A drop of blue dye solution was introduced onto the filter paper through the small hole on the film. Since water vapour could only escape from the small hole, which was above the centre of the solution-wetted area, this experimental design suppressed the higher water evaporation rate at the edge of the solution-wetted area.

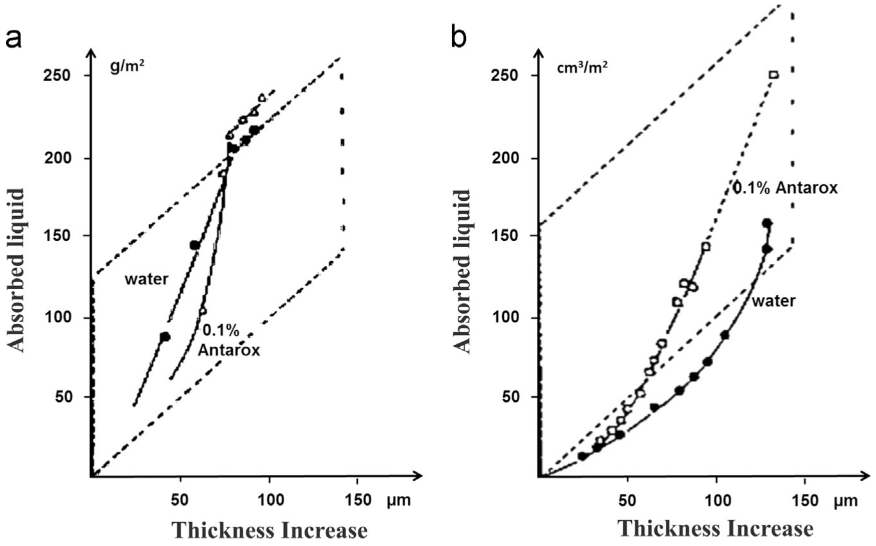

Fig. 1. Absorbency rate of liquid transport through (a) hydrophilic and (b) hydrophobic paper (Antarox is an alkoxylated alcohol non-ionic surfactant which increase wetting of aqueous liquid with paper. A 0.1% Antarox aqueous solution has a greater penetration rate in paper than water; it can penetrate throughout the fibre network in shorter time. A shorter liquid–fibre contact time causes less fibre swelling. The Antarox solution was employed to demonstrate the situation in which liquid penetrates in a less-swelling fibre network.). Figure reproduced with permission (Bristow and Kolseth, 1986), Marcel Dekker.