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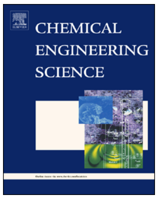

An experimental study on dynamic pore wettability

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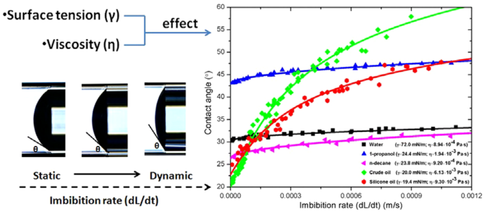
HIGHLIGHTS

- We develop a technique to experimentally measure dynamic pore contact angle.
- Dynamic pore contact angle increases monotonically with the contact-line velocity.
- Surface tension and viscosity affect the dynamic pore contact angle significantly.
- A new empirical correlation developed can predict dynamic wetting in a small pore.
- The dynamic contact angle results are correlated with the Crispation number (Cr).

GRAPHICAL ABSTRACT



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ABSTRACT

Dynamic pore wettability is important for understanding fluid behavior and adsorption in porous media for enhanced oil recovery, groundwater movements, nanofluidics and nanolubrication. Although dynamic wetting of different liquids has been extensively studied on various plane substrates, dynamic wettability in small pores has not been systematically investigated. In this paper, we measured dynamic contact angles in single glass capillaries with a size range from 100 to 250 μm, in order to investigate the relationship between dynamic contact angle and spontaneous imbibition of various liquids, the effects of surface tension and viscosity of liquids on dynamic contact angle, and the dependence of contact angle on contact-line velocity in a pore. The liquids used are silicone oils with various viscosities, deionized water, 1-propanol, n-decane, crude oil, propanol-water mixtures with various surface tensions. The results indicate that the dynamic contact angle of liquids in a pore increases monotonically with the contact-line velocity at low capillary numbers, and this increase becomes more significant when more viscous liquids or liquids with lower surface tensions are used. A new empirical correlation based on the obtained experimental data has been proposed to describe dynamic pore wettability in a low capillary number range ($1.0 \times 10^{-7} < \mathrm{Ca} < 1.8 \times 10^{-5}$). Finally, we show that all our results can be summarized by a master curve relating the contact angle variation at a specific velocity with the Crispation number (Cr) signifying the importance of the interfacial deformation of liquid in a pore.

1. Introduction

Dynamic wetting is a feature of the motion of liquid–liquid or liquid–gas interfaces in porous media, and is of significant importance

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in ceramic, coating, printing, detergency, groundwater movements, soil science and oil recovery (Cazabat, 1992; de Gennes, 1985; Dussan, 1979; Elyousfi et al., 1998; Ishimi et al., 1998; Teletzke et al., 1987, 1988), nanofluidics and nanolubrication (Martic et al., 2005). Dynamic wettability is characterized by dynamic contact angle (Latva-Kokko and Rothman, 2005) and is mainly measured through the spreading of liquids onto flat solid surfaces. For instance, Bayer and Megaridis (2006) measured dynamic contact angles during the spontaneous spreading and recoiling of water droplets on flat surfaces with various wetting conditions. Keller et al. (2007) used the Wihelmy plate technique to measure the dynamic contact angles of petroleum hydrocarbons at various advancing velocities. Previous research on flat surfaces has indicated that dynamic contact angle depends on the speed of solid–liquid–gas contact line, and varies with drop volume, viscosity, surfactant concentration, flow geometry, fluid composition and solid surface properties (Carré and Eustache, 1997, 2000; Dezellus et al., 2002; Min et al., 2011; Roques-Carmes et al., 2010; Wang et al., 2007).

Dynamic wetting of liquids can be described by several theories such as the hydrodynamic theories proposed by Cox (1986), Voinov (1976), Dussan (1976) and the molecular-kinetic theory introduced by Blake and Haynes (1969). Combined models have also been attempted to describe contact line motion of spreading liquids by Petrov and Petrov (1992). A number of empirical correlations (Jiang et al., 1979; Bracke et al., 1989; Seebergh and Berg, 1992) and semi-empirical correlations (Rillaerts and Joos, 1980; Ishimi et al., 1986; Ström et al., 1990) have been proposed to predict the dynamic contact angle (θ_d) by using the static contact angle (θ_s) and the capillary number (Ca). The capillary number (Ca) is defined as the ratio of viscous forces to interfacial forces. For instance, Jiang et al. (1979) presented an empirical correlation to describe the dependence of dynamic contact angle on capillary number (Ca) and static contact angle (θ_s) based on Hoffman's data through a study of non-polar liquids spreading. Bracke et al. (1989) gave a similar empirical correlation by drawing polymer strips into liquid. Because Ca and θ_s can be easy to measure, the correlations from Jiang et al. (1979) and Bracke et al. (1989) can be applied to most of three-phase dynamic wetting phenomena when capillary number is less than 0.01. Seebergh and Berg (1992) examined the dynamic contact angle at a low capillary number regime via force measurements by using a dynamic microtensiometer. The correlations proposed by Seebergh and Berg (1992) is a function of contact-line velocity, and have the same functional form as the correlations from Jiang et al. (1979) and Bracke et al. (1989) at low capillary numbers, but with different constants.

In most of dynamic contact angle studies, the Lucas–Washburn equation is often used to calculate the contact angle in a pore using measured capillary imbibition distance and imbibition time (Chibowski and Hoysz, 1997; Martic et al., 2002; Siebold et al., 2000; Xue et al., 2006), but the contact angle calculated from Lucas–Washburn equation is static. To describe the imbibition dynamics, Joos et al. (1990) used velocity-dependent contact angle (θ_v) which was derived from an empirical expression to replace the static contact angle (θ_s) in the classic Lucas–Washburn equation. Martic et al. (2002) modified the classic Lucas–Washburn equation by using Blake's molecular-kinetic theory. Succi group used the molecular-kinetic model to describe the micro-capillary imbibition dynamics considering the friction effect on the three-phase moving line, and the modeling results matched the experimental data well (Girardo et al., 2012). Stukan et al. (2010) investigated the effect of roughness on the spontaneous imbibition of liquid in nanopores by coarse grain molecular dynamics simulation and used the Blake's molecular-kinetic theory to describe the effect of dynamic contact angle on liquid imbibition. Because of lack of experimental techniques to measure the dynamic contact angle in a small pore, most of the experimental or theoretical works on dynamic wettability were based on the data measured from a flat solid plate, strip or cylindrical rod rather than in pores (Seebergh and Berg, 1992). It is commonly assumed that the contact angle on a flat surface can represent the wetting condition in a pore. This might be true in some cases but deserves to be assessed (Gomez et al., 2000). So, it is crucial and necessary to directly measure dynamic contact angles in a pore to advance the understanding of dynamic multiphase interfaces advancing through the porous medium.

In this paper, dynamic wetting behavior in a pore was studied in a low capillary number regime from 10^{-7} to 10^{-2}. Since an ensemble of single pores with simplified geometries is accepted as representation of pore system (Friedman, 1999), the main objectives of this work were therefore to directly measure the dynamic contact angles for various liquids imbibed into single glass capillaries in order to describe the dependence of dynamic contact angle on imbibition rate. The results showed the effects of surface tension and viscosity of liquids on the dynamic contact angle in a pore, which were well explained by the Crispation number (Cr). A new empirical correlation was developed to describe the dynamic wetting in a pore in a low capillary number regime.

2. Theories and equations

2.1. Hydrodynamic and molecular-kinetic theories

The dynamic wetting can be described by the hydrodynamics models proposed by Cox (1986), Voinov (1976), Dussan (1976) and Blake's molecular-kinetics theory (Blake and Haynes, 1969). The hydrodynamic theory and molecular-kinetic model consider dissipation effects during imbibitions due to the viscous friction in the bulk and to the solid characteristics at the moving contact line, respectively (Girardo et al., 2012). According to the hydrodynamic model, the spreading process is dominated by viscous dissipation. Viscous friction in the bulk is the controlling mechanism for the motion of the contact line. Cox–Voinov equation is a simple description of the contact line motion and the driving force (deviation of the contact angle from equilibrium) (Cox, 1986; Voinov, 1976):

$$v=\frac{\gamma}{9\eta\,\ln\left(\frac{\ell}{a}\right)}\left(\theta_d^3-\theta_s^3\right) \tag{1}$$

where θ_d is the dynamic contact angle, θ_s is the static (equilibrium) contact angle, η is the liquid viscosity and γ is the liquid–vapor interfacial tension. ℓ/a is the ratio of macroscopic to microscopic length scales. Brochard-Wyart and de Gennes (1992) derived an equivalent expression by considering the spreading as an irreversible process and calculating the energy dissipation per length of unit line. The velocity of the contact line is then given by:

$$v=\frac{\theta\gamma}{6\eta\,\ln\left(\frac{\ell}{a}\right)}\left(\cos\,\theta_s-\,\cos\,\theta_d\right) \tag{2}$$

Blake developed a molecular-kinetic theory of three-phase moving line based on Eyring's activated-rate theory with an adsorption/desorption model (Blake and Haynes, 1969). The imbibition rate (penetration velocity) is given by:

$$v=\frac{dL}{dt}=2K_0\lambda\,\sin\,h\left[\frac{\gamma(\cos\,\theta_s-\,\cos\,\theta_d)}{2nk_BT}\right] \tag{3}$$

Where K_0 is the frequency of molecular displacement, n denotes adsorption sites per unit area ($n^{-1}=\lambda^2$), λ is the average length of each molecular displacement, T is the temperature and k_B denotes Boltzmann constant ($k_B=1.381\times10^{-23}\,\mathrm{J\,K^{-1}}$). The term of $\gamma(\cos\,\theta_s-\,\cos\,\theta_d)$ can be regarded as the nonequilibrated surface tension force to drive the motion of the wetting line.