Experimental measurement of forces and energies associated with capillary rise in a vertical tube

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ABSTRACT

We examined the forces and energies associated with liquid rising in a capillary tube. Glass and polytetrafluorethylene (PTFE) tubes with diameter ranging from 0.5 to 1.4 mm were brought into contact with ethylene glycol, glycerol or silicone oil to initiate rise. We measured the force generated by the rising liquids with a tensiometer and plotted them against rise height. From these plots, we estimated the change in potential energy. For a given liquid–solid combination, the change in potential energy was equal to the difference between the work of wetting and viscous dissipation in the bulk of the liquid; potential energy values were independent of tube diameter and ranged from 7 mJ/m^2 for silicone oil rising through PTFE to 33 mJ/m^2 for glycerol and glass.

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1. Introduction

Contact angle measurements and estimates of the work of wetting are used widely to assess the potential for creating a high strength adhesive bond [1]. The most common of these methods involve sessile drops, which are well suited for flat surfaces [2,3]. However, sessile drop measurements and their interpretation on small, curved geometries can be challenging.

Alternatively, tensiometers are used to evaluate small, curved solids, such as fibers. Here, the solid is immersed or withdrawn from a liquid while measuring force [4]. Proper analysis of the interplay between capillary forces and buoyancy allows for indirect estimation of contact angles [5,6].

While traditional tensiometry may work well for small, solid objects, it may not be well suited for capillary tubes or hollow fibers. During immersion or withdrawal, liquid may contact both the inner and outer diameters. Also, rise inside the tube can complicate interpretation. Therefore, in many cases, this technique does not readily allow one to distinguish the wettability of the inside of tubes.

In this study, we have developed a new technique for evaluating the wettability and work of wetting inside capillary tubes and hollow fibers. We used a tensiometer, but in an unconventional way. We did not immerse and withdraw our tubes, but just contacted the surface of the liquid. We simultaneously measured force, time and location of the rising liquid. We isolated the forces from liquid rising inside the tube and then used those values to estimate work, viscous dissipation and potential energy change. As we discuss in greater detail later, our measurements are analogous to tensile elongation of a solid.

2. Theory

2.1. Capillary rise

Consider the vertical capillary tube of internal diameter D shown in Fig. 1. The capillary is brought into contact with a liquid of surface tension γ_l, density of ρ, and viscosity of μ, such that its bottom just touches the liquid, Fig. 1a. A meniscus forms around the inner and outer diameter of the capillary. The meniscus wets the tube with an advancing contact angle of θ, which is assumed to remain constant with both time and position. The liquid inside the capillary immediately begins to rise in the vertical or z direction, rapidly at first and then slows Fig. 1b. The time (t) required to reach a height of z can be approximated by the Lucas–Washburn equation [7–9],

$$t = \frac{-128 \cdot \gamma_l \mu}{\rho^2 g^2 D^3} \left[\frac{\rho g D z}{4\gamma_l} + \cos\theta \cdot \ln\left(1 - \frac{\rho g D z}{4\gamma_l \cos\theta}\right) \right] \quad (1)$$

where g is the acceleration due to gravity. Eventually, the liquid reaches a final height (h) where the liquid stops, Fig. 1c. If the diameter of the capillary is sufficiently small such that $h \gg D$, then the ultimate height (h) of liquid rise can be estimated as [10–13]

$$h = \frac{4\gamma_l \cos\theta}{\rho g D} \quad (2)$$

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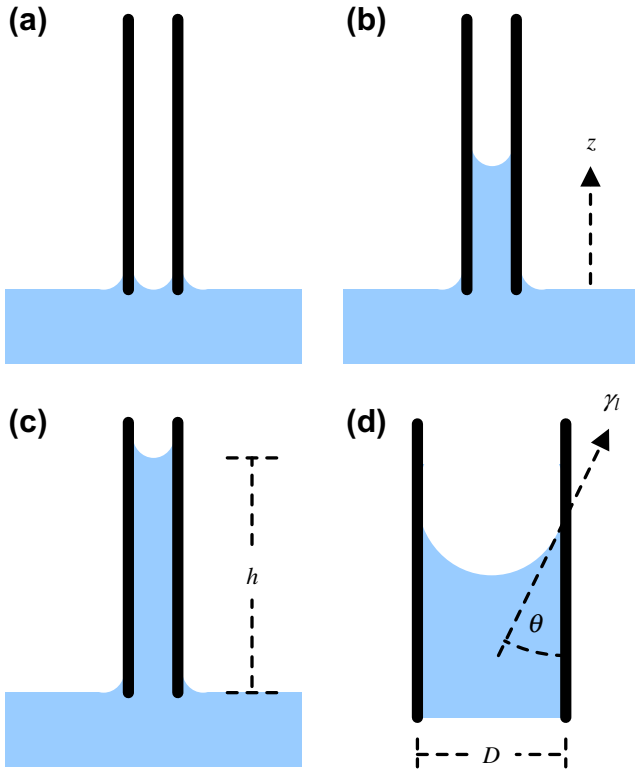   *E-mail address:* chuck_extrand@entegris.com (C.W. Extrand).

Fig. 1. A depiction of capillary rise in a small diameter tube: (a) the tube contacts the liquid, (b) liquid rises vertically inside the tube, (c) the liquid stops at an equilibrium height of h, and (d) a close-up view of the meniscus.

2.2. Forces and energies

For both measurements and predictions, we need several working equations, which are derived below. Brown [14] was the first to theoretically examine energies associated with liquid rising in a capillary tube. Others have followed his approach [15–22]. The energy balance for capillary rise consists of the three terms: the work done in lifting the liquid (w), a kinetic energy term that represents viscous dissipation (K) in the bulk of the flowing liquid and a potential energy term that accounts for energy stored in the liquid column,

$$w - K = -\Delta U \tag{3}$$

Our derivation below is similar to Brown's [23], except that we assume that the motor for the liquid rise originates from molecular interactions in the vicinity of the contact line [24], rather than from free energy changes within the liquid–solid interface.

Let us begin with the potential energy, as this is a quantity that we can obtain directly from tensiometry measurements. According to elementary thermodynamics [25], the change in the potential energy ($-\Delta U$) can be calculated by integrating the hydrostatic force (f_i) acting on the inside of tube as liquid rises from $z = 0$ to $z = h$,

$$-\Delta U = \int_0^h f_i \cdot dz \tag{4}$$

The hydrostatic force is the product of the local hydrostatic pressure (Δp) and the cross-sectional area of the tube (A_c), which in turn can be framed in terms of tube diameter, liquid density and height,

$$f_i = \Delta p \cdot A_c = \frac{\pi}{4}\rho g D^2 z \tag{5}$$

Combining Eqs. (4) and (5) and then integrating produces an expression for the change in potential energy due to capillary rise [14],

$$-\Delta U = \int_0^h \frac{\pi}{4}\rho g D^2 z \cdot dz = \frac{\pi}{8}\rho g D^2 h^2 \tag{6}$$

The energy lost due to viscous dissipation (K) for laminar flow through a tube of constant cross section generally can be estimated from the liquid volume (V) and pressure change (Δp) [26],

$$K = \int_0^{\Delta p} V \cdot d(\Delta p) \tag{7}$$

For capillary rise, Eq. (7) becomes [14]

$$K = \int_0^h \frac{\pi}{4}\rho g D^2 z \cdot dz = \frac{\pi}{8}\rho g D^2 h^2 \tag{8}$$

The work done as surface tension lifts liquid upward through a tube (w) can be calculated by integrating the capillary force (f_c) from $z = 0$ to $z = h$,

$$w = \int_0^h f_c \cdot dz \tag{9}$$

where f_c is the product of length of the contact line and the vertical component of the surface tension,

$$f_c = \pi D \gamma_l \cos\theta \tag{10}$$

Combining and integrating gives

$$w = \pi D h \gamma_l \cos\theta \tag{11}$$

Now that we have derived these three quantities, $-\Delta U$, w and K, we can use them to do several things. Firstly, we can combine Eqs. (3), (6), (8), and (11), then solve for h to obtain the well-known expression for capillary rise, Eq. (2). This approach is simpler and less circuitous than the route of Brown [14], which requires use of the Young equation and the assumption that wetting is driven by changes of solid surface energy.

Secondly, we can define several intrinsic quantities that will be useful in our analysis of energies associated with capillary rise. The wetted area (A) of the inside of the capillary is

$$A = \pi D h \tag{12}$$

Subsequently, the change in potential energy per wetted area ($-\Delta U/A$) is

$$-\frac{\Delta U}{A} = \frac{1}{8}\rho g D h \tag{13}$$

We also can define the work per wetted area (W) as

$$W = \frac{w}{A} = \gamma_l \cos\theta \tag{14}$$

Additionally,

$$\frac{w - K}{A} = \gamma_l \cos\theta - \frac{1}{8}\rho g D h \tag{15}$$

By substituting Eq. (2) for h into Eq. (15) gives

$$\frac{w - K}{A} = \frac{1}{2}\gamma_l \cos\theta \tag{16}$$

Thus, from Eq. (3), we anticipate that one-half the work per wetted area is converted into potential energy

$$-\frac{\Delta U}{A} = 1/2 W \tag{17}$$

3. Experimental details

The liquids used in the experiments were ethylene glycol (Sigma–Aldrich, anhydrous 99.8%), glycerol (Aldrich, >99%, GC), and silicone oil (Aldrich, AP 100, polyphenyl-methylsiloxane). The