



Experimental and theoretical investigation of contact-angle variation for water–ethanol mixture droplets on a low-surface-energy solid



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ABSTRACT

Consider a situation where a droplet is deposited on a solid surface. If the droplet volume decreases, the droplet exhibits complex behavior, such as hysteresis and size dependence of its contact angle. In this study, we perform experimental and theoretical studies of the wettability of water–ethanol droplets on a low-surface-energy solid. In the experiment, the droplet behavior is examined with decreasing volume as a result of microsyringe extraction or natural evaporation. In particular, we analytically model the adsorption of liquid molecules at the solid–liquid interface and the change in the surface energy density of the liquid during the volume-change process. These models are validated with experimental data. From the experimental results, the droplet behavior resulting from microsyringe extraction and natural evaporation differ considerably with increasing ethanol concentration. Our results suggest that the complex behavior of the droplets during the volume change is related to liquid molecules adsorbed at the solid–liquid interface and the change in the surface energy density of the liquid induced by the concentration change resulting from evaporation of the binary liquid mixture near the contact line.

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1. Introduction

When the volume of a droplet deposited on a solid surface decreases, the contact angle decreases from its equilibrium value while the contact area remains constant. Until the contact angle reaches a certain value, the contact line is pinned. This behavior is known as contact angle hysteresis. When the contact angle finally reaches a specific value, the contact line de-pins and starts to recede. Eventually, the contact angle approaches zero as the contact area radius decreases. This behavior is known as the size dependence of the contact angle. Contact line pinning and de-pinning is also observed during processes where the contact line recedes (i.e., stick–slip motion). This sequential droplet behavior has also been observed in experimental studies using binary liquid mixtures at low ethanol concentrations [1]. Regarding the stick–slip behavior, Shanahan and Sefiane suggested a concept based on a pinning force at the contact line [2,3]. According to their concept, the process is affected by a potential barrier at the contact line. Based on the Shanahan–Sefiane model, quantitative evaluation of the pinning force and contact line behavior, including stick–slip motion, is discussed in Ref. [4]. The line tension concept

is a popular way [5–13] to explain the contact angle size dependence, but it does not consider stick–slip behavior. In the modified Young equation, the line tension is added into the conventional Young equation, and it is estimated by fitting the modified Young equation to experimental data relating the radius of curvature of the contact line and the cosine component of the contact angle. It has been suggested that the line tension is negative and constant [14]. However, contact angle and size dependences, and positive and negative line tensions have been widely reported [15–20]. Recently, it has been reported that the line tension approach is a fitting method that considers macroscopic physical values, such as the gravitational potential of droplets, as a single parameter (i.e., line tension). The sign of the line tension can be related to the gravitational potential of existing large droplets, and the sine component of the surface tension [21]. This suggests that the size dependence of the contact angle must be considered from a different perspective. From a physicochemical point of view, these two characteristic behaviors are considered to result from adsorption of liquid on the solid surface. Extrand developed a contact angle hysteresis model based on the physicochemical notion of adsorption–desorption [22]. In this model, hysteresis is modeled by associating the free energy difference with the advancing and receding contact angles. The free energy difference involved in contact angle hysteresis for various polymer surfaces was analyzed. A physicochemical interpretation related to contact

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angle hysteresis has also been reported recently [23]. The size dependence of the contact angle is explained without the concept of line tension and considering vapor adsorption at the solid–gas interface [24]. In this study, water-droplet wettability on solid surfaces under specific conditions, such as a saturated vapor environment, was considered. Size dependence of the contact angle was observed by controlling the vapor pressure in a confined vessel and numerically analyzed based on a rigorous thermodynamic model [25]. Besides the adsorption concept, there are some reports that indicate that the surface heterogeneity of a solid surface may be related to the size dependency of the contact angle [26–28]. It has been reported that the line tension concept cannot explain the size dependence of the contact angle in small droplets [26].

There are also some interpretational issues: the relationship between size dependence and contact angle hysteresis is unknown and a definite solution of this phenomenon is still missing. Considering that wetting originates from intermolecular interactions between liquid and solid surfaces, a physicochemical description, such as liquid-to-solid surface adsorption, may give a consistent interpretation to these two characteristic behaviors. From this point of view, we herein develop an analytical model that can treat the sequential change in the contact angle caused by volume reduction, focusing on adsorption at the solid–liquid interface and the concept of the work of adhesion. In particular, we performed wettability experiments on a low-surface-energy solid using a water–ethanol liquid mixture with high ethanol concentration under ambient conditions at constant temperature and humidity. The validity of the analytical model is then discussed based on the experimental data. Our model indicates that complex droplet behavior may be related to the adsorption of liquid molecules at the solid–liquid surface and changes in the surface energy densities of the liquid and the solid–liquid interface. This study provides some understanding of the relationship between hysteresis and size dependence of the contact angle for droplets on a low-surface-energy solid and, as such, will be important in industrial applications from an engineering perspective.

2. Theory

The contact angle of a water–ethanol droplet on a solid surface at low ethanol concentrations exhibits complex behavior as the droplet volume changes [1]. Focusing on the relationship between the contact angle and the contact area radius, there are two main characteristic behaviors, as schematically shown in Fig. 1. One is contact-angle hysteresis (the process from A to B), and the other is the size dependence (the process from B to C). In the following

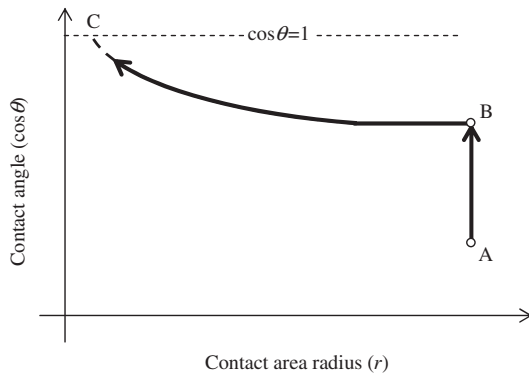


Fig. 1. Schematic plot of the relationship between the contact area radius and the contact angle during a volume change. At point A, the droplet is initially deposited on the solid surface. Point B is the transition point where the contact line starts to recede. Then, the droplet dries out at point C.

section, the two processes (A–B and B–C) will be modeled. The model is then compared with experimental observations of natural droplet evaporation that corresponds to the sequential process from A to C. Here, the natural evaporation process is considered to be at a quasi-equilibrium state [29–32] since the time required for the vapor concentration to adjust to the changes in the shape of the droplet—given by $t_D = r^2/D$, where r is the initial contact area radius and D (equal to $2.32 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ [33]) is the diffusivity of water vapor in air—is five orders of magnitude smaller than the total evaporation time (t_f). In addition, for the case of pure ethanol, t_D/t_f is on the order of 10^{-3} , where $D = 1.21 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ [34]. As this value is small enough, the droplet behavior of the binary liquid mixture can be assumed to be at a quasi-equilibrium state.

2.1. Contact angle hysteresis

First, we model contact angle hysteresis focusing on liquid adsorption at the solid–liquid interface. The concept of critical surface tension (σ_{crit}) is used in the present study to characterize the solid surface [35] because the direct measurement of the surface energy density of the solid is very difficult.

At point A in Fig. 1, when the droplet is initially deposited on a solid surface (see Fig. 2(a)), equilibrium conditions prevail and the Young equation holds:

$$\sigma_{\text{sg}}^A = \sigma_{\text{sl}}^A + \sigma_{\text{lg}}^A \cos \theta^A, \tag{1}$$

where θ is the contact angle of the droplet and σ_{sg} , σ_{sl} , and σ_{lg} are the surface energy densities of the solid–gas, solid–liquid, and liquid–gas interfaces, respectively. In the present study, superscript labels A, B, and C indicate that the quantities are evaluated at the given point, i.e., A in Eq. (1). For aqueous solutions on low-surface-energy solids, the relationship among the contact angle, critical surface tension, and surface energy density of the

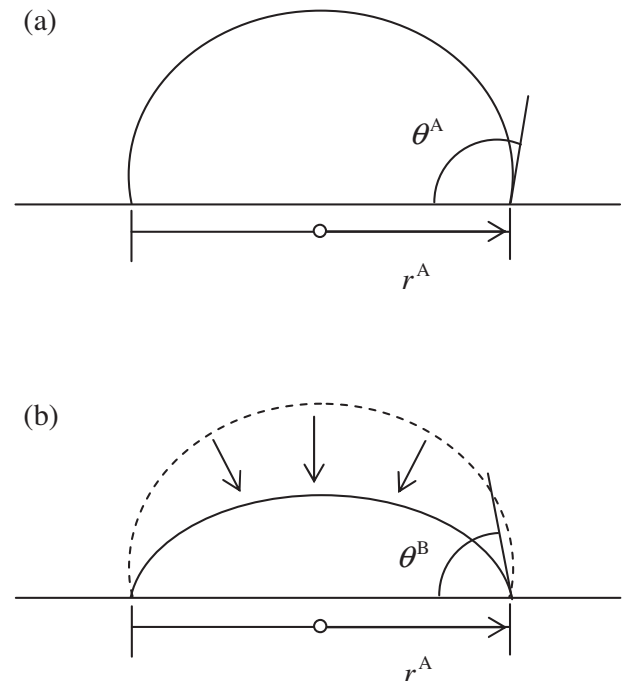


Fig. 2. Schematic diagram of a droplet showing the change of the contact area radius and contact angle under a volume change corresponding to (a) point A and (b) point B in Fig. 1.

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