SPREADING OF LIQUID DROPS ON ACRYLIC SURFACES

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Abstract. *Wettability is a physical-chemistry property with a strong influence in liquid-fluid-solid system. It can be defined as the degree of affinity between a liquid and a solid surface. A method used for measuring the wettability is based on the contact angle, defined as the angle formed between the line tangent to the liquid-fluid interface and the line parallel to the solid surface. In this work, an experimental study was carried out by analyzing the spreading of water drops on an acrylic polished surface, both immersed in mineral oil (Nujol) and maintained at the temperature of 20 Celsius degrees. An optical goniometer was used to capture the images and calculate the contact angles. In the experiment, a water drop is deposited over a previously treated acrylic surface. The drop spreading is monitored and recorded for a long period of time until the system does not suffer any change in its configuration, allowing the measurement of the contact angle step by step and the study of the water-oil-acrylic interaction under static and dynamic conditions. Some preliminary results are compared with those found in the literature.*

Keywords*: spreading, wettability, contact angle, acrylic.*

1. INTRODUCTION

Wettability is a physical-chemistry property which has a strong influence in systems where the contact between fluids and surfaces can be observed. This property is involved in several nature phenomena, as the rise of underground water in soils and water transport from the roots to the leaves in trees. Many industrial and technological applications are dependent of this property, including oil recovery from porous rocks, coating and lubrication processes. Through the wettability, surfaces can be characterized and interactions in solid-fluid-liquid systems can be determined (Johnson and Dettre, 1993).

The purpose of this work is to study the interaction of liquids, as water and mineral oil (Nujol), when they are put in contact with an acrylic surface, since such material is used to build representative and simplified micromodels**,** where the immiscible displacement of fluids in porous media can be visualized. In this context, the wettability has a fundamental role.

Generally, wettability is defined as the degree of affinity between a liquid and a solid surface under controlled environment conditions. A method used for measuring the wettability is based on the contact angle, defined as the angle formed between the line tangent to the liquid-fluid interface and the line parallel to the solid surface and illustrated in Fig. 1 (Lyklema, 2000). For a liquid with a stronger interaction with a given surface, the contact angle will be smaller.
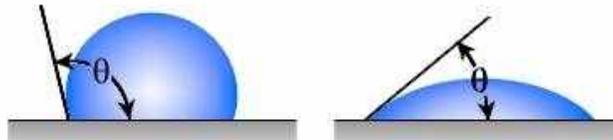

Figure 1. Contact angle measurements.

When a liquid drop is put on a solid surface, like in Fig. 1, the liquid-fluid-solid system exhibits in its configuration three different interfaces: liquid-fluid, solid-fluid and liquid-solid. Due to the intermolecular forces acting in each interface, it is observed the presence of adhesive and cohesive forces. Adhesive forces stimulate the spreading of the drop, while the cohesive forces induce the drop to come back to its spherical shape. The contact angle is determined by the competition between these two forces (Johnson and Dettre, 1993). Under equilibrium conditions, it is possible to get a relationship between the *static* contact angle and the interfacial tensions (see Fig. 2). This relationship is known as Young-Dupré equation (Young, 1805; Dupré, 1869), given by

$$\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} = \cos\theta_0 , \qquad\qquad (1)$$

where γ_{SV}, γ_{SL}, γ_{LV} are the solid-vapor, the solid-liquid and liquid-vapor interfacial tensions and θ_0 is the static contact angle.
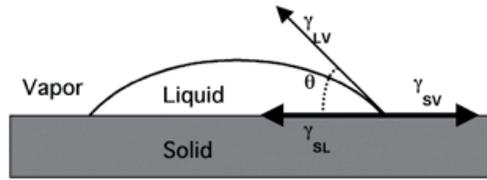
Figure 2. Interfacial tensions and contact angle for a drop on a solid plate.

We restrict ourselves to systems where the capillary forces are dominant with respect to gravity. For such systems is supposed that under *capillary regime* any influence of the gravity on the contact angle measurement is negligible. This is supposed to be valid when the drop basis radius, *r*, is smaller than the capillary length, *a*:

$$a = \sqrt{\frac{\gamma_{LV}}{\rho_L g}} \tag{2}$$

where ρ_L is the density of the liquid and *g* is the acceleration of gravity. The opposite case, when $r > a$, is refereed to as the *gravity regime* (de Gennes et al., 2003).

2. MATERIALS AND METHODS

The experimental study was carried out with an optical goniometer, provided by Dataphysics Instruments, that allows the capture and analysis of images of the water and mineral oil drops deposited over the acrylic substrate (Zosel, 1993), as shown in Fig. 3. The contact angle was measured by the sessile drop method (Cheng et al., 1990), in which a theoretical drop, calculated from a special form of the Young-Laplace equation, is fitted to the experimental one. The syringe plunger is controlled electronically, and then a drop with a predefined volume in the needle can be produced. After that, the drop is brought very slowly near the surface until touching it, leaving the needle and spreading on the solid surface.
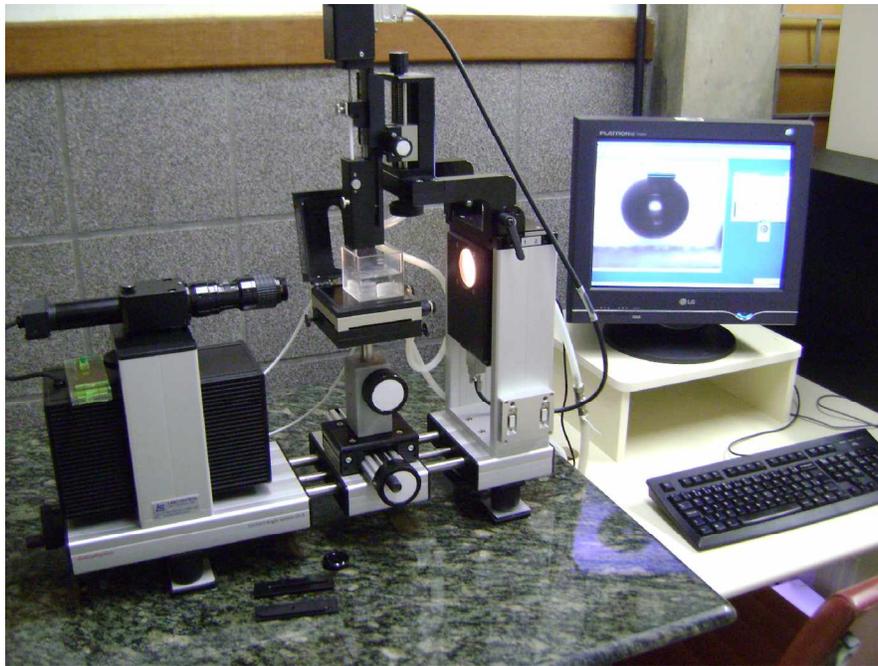

Figure 3. Experimental set up.

In the experiment, the drop is deposited on the acrylic surface and allowed to spread until the equilibrium is reached. All drop evolution is firstly recorded, enabling the pos-processing analysis after the conclusion of the experiment. This can be done for several drops, increasing the sampling and reliability of the results. From each drop record, it is possible to obtain the time evolution of different geometrical parameters associated to the drop, as contact angle, base diameter, volume and height (Zosel, 1993). Therefore, the study of the water-oil-acrylic interaction under different conditions can be performed

easily. As the drop spreading is a fast process, specially at the first steps succeeding the liquid-solid contact, the camera is adjusted to take pictures using a frame rate of around 25 images per second, anyway such frame rate is incapable to capture appropriately all the process, since water is a low-viscosity fluid. The experiments were performed at a temperature of 20 °C. In order to minimize contamination effects, all the parts used, like glassware, syringes, needles and acrylic plates, were washed with detergent and water, immersed in a solution of potassium hydroxide (KOH) and Ethanol and aqueous solution of Nitric Acid, cleaned by ultrasonic bath, rinsed with deionized and distilled water, and dried in a drying stove. Before cleaning, the acrylic samples were polished, in a randomly way, with a colloidal suspension of 0.06 μm particles. In some cases, it was observed that the liquid spreads on the outside surface of the needle, avoiding the correct formation of well-defined drops. In such cases, a layer of hydrophobic coating was applied to the needle tips.

3. RESULTS AND DISCUSSION

In this work, three different systems were studied. The liquid-fluid-solid systems studied were water-air-acrylic, oil-air-acrylic and water-oil-acrylic.

For the water-air-acrylic system, the drop of water was observed to spread faster at the beginning, slowing down after about 60 seconds. As water is a volatile liquid and the relative humidity of the environment atmosphere was not controlled, the drop volume and contact angle decreases along the time, as shown in Fig. 4. In this figure, it can be observed that the basis diameter was almost stabilized after 200 seconds, while the contact angle continued to decrease, as a result of the high evaporation. Nevertheless, although the basis diameter oscillates, one can expect that the drop volume diminishes isotropically, like a spherical cap, in which the contact angle would be kept constant in the same manner that the drop diameter, what did not happen in this case. This phenomena is known as pinning of the contact angle (de Gennes, 1985), since the acrylic plate is not smooth at the microscopic scale.
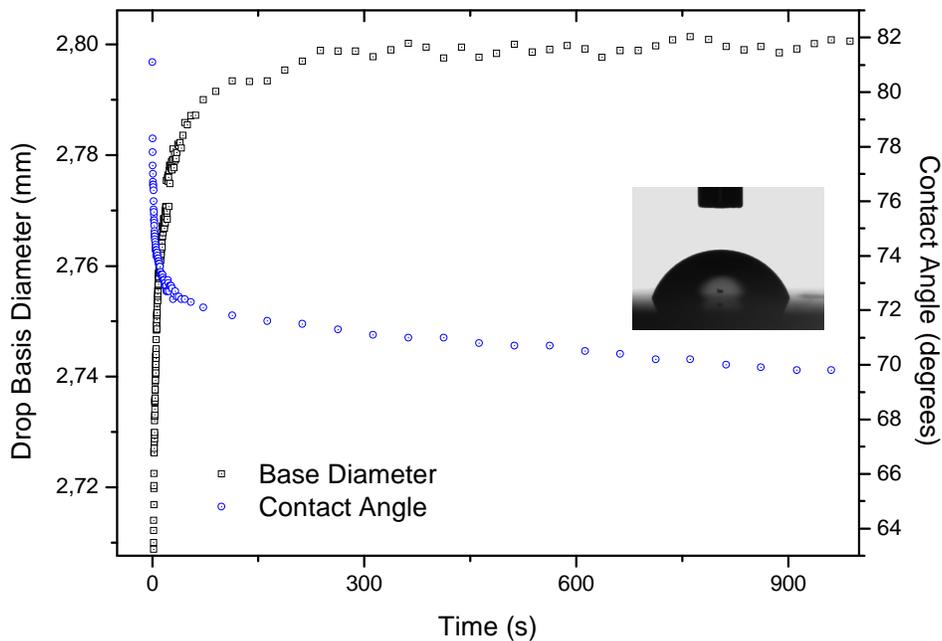

Figure 4. Contact angle and drop basis diameter as a function of the time.

Since it was not possible to avoid the evaporation of the water during the experiments, the static contact angle was determined after the stabilization of the drop basis diameter. The value of water-air-acrylic contact angle was measured to be $70.4 \pm 0.3°$.

In a second experiment, the contact angle in an oil-air-acrylic system was measured (see Fig. 5). Since the oil is less volatile than water, it is easier for measuring the contact angle in this experiment with respect to the first. The static contact angle for this system was measured to be equal to $25 \pm 3°$.
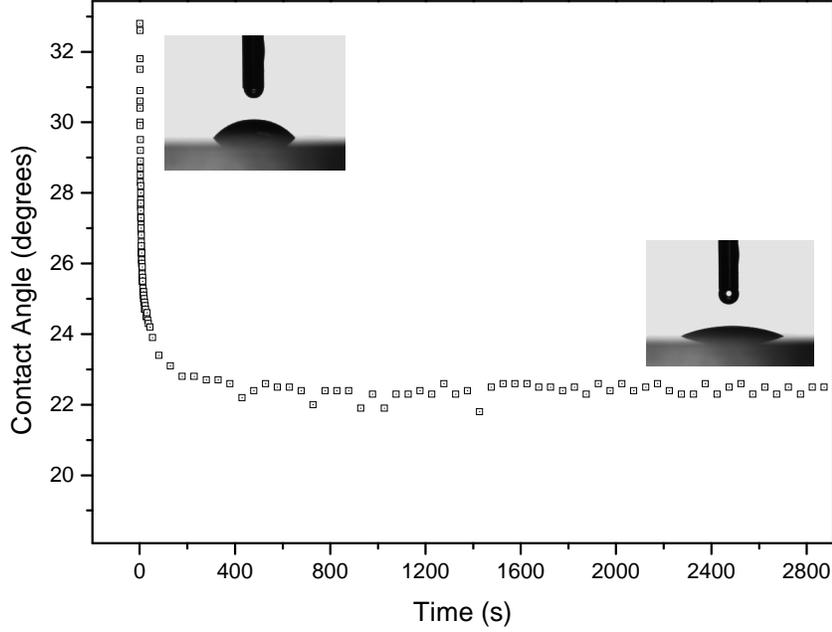
Figure 5. Contact angle as a function of the time for the oil-air-acrylic system.

For non volatile liquids, the dynamics of partial wetting systems, which do not exhibit a zero contact angle, spontaneously spreading, follows approximately a universal behavior and the dynamic contact angle can be written in terms of the capillary number (Ca), given by

$$Ca = \frac{V\mu}{\gamma_{LV}},$$ (3)

which is the ratio between viscous and capillary forces. In the relation above, V represents the spreading velocity and μ is the absolute viscosity.

Jiang et al. (1979) described this universal behavior for the dynamic contact angle following the characteristic function, H:

$$H \equiv \frac{\cos\theta_o - \cos\theta_D}{\cos\theta_o + 1} = \tanh(4.96 Ca^{0.702})$$ (4)

where θ_D is the dynamic contact angle.

Bracke et al. (1989) proposed another expression for H

$$H \equiv \frac{\cos\theta_0 - \cos\theta_D}{\cos\theta_0 + 1} = 2\sqrt{Ca}$$ (5)

Three different experiments were performed to obtain an approximation for the function H, which characterizes the water-oil-acrylic system. For each experiment, the following theoretical curve was fitted to the experimental points:

$$H \equiv \frac{\cos\theta_0 - \cos\theta_D}{\cos\theta_0 + 1} = mCa^n$$ (6)

where m and n are constants that are calculated by the best-fitting process.

Drop	Constant m	Constant n	R^2
1	3.91374	0.52576	0.99004
2	3.80386	0.55937	0.98907
3	2.63541	0.47144	0.98187

Table 1. Constants calculated by the best-fitting process.

The obtained results are shown in Fig. 6 and Tab. 1. The coefficient of determination R^2, which represents how well the regression line approximates the real data points, was measured and results close to 1.0 were obtained. An R^2 of 1.0 indicates that the regression line perfectly fits the data.

Taking the mean values of the constants m and n, it is possible to describe the dynamics of spreading for the oil-air-system though the following relationship:

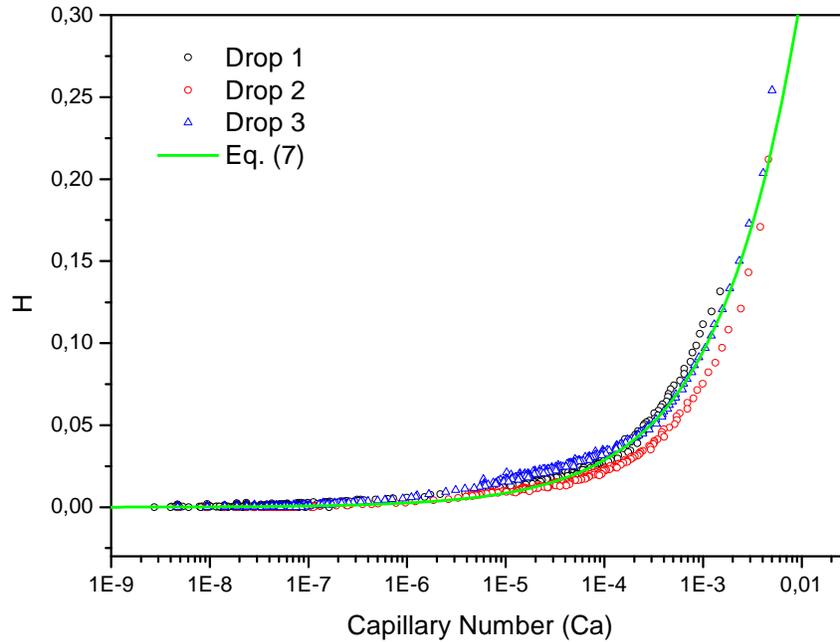$$H \equiv \frac{\cos\theta_0 - \cos\theta_D}{\cos\theta_0 + 1} = 3.45 Ca^{0.52} \tag{7}$$

Figure 6. Characteristic function H as a function of the capillary number.

As it can be seen, the dynamics of spreading for the studied cases follows approximately the spreading behavior reported by Bracke et al. (1989).

In a third experiment, the dynamics of the spreading of a drop of water was followed when this drop was immersed in a mineral oil bath. In the water-oil-acrylic system, it is easier to observe the first steps of the spreading process after the water drop was deposited on the solid surface, displayed in Fig. 6. Beyond that, all the dynamic process is slower than the one happening in air, since the absolute viscosity of mineral oil at 20°C is around 150 higher than the water viscosity. As a result, the equilibrium state is only reached after 4-5 hours. In this case, the water drop was monitored for around 5 hours and the static contact angle for the system was measured to be $101.8 \pm 0.8°$.
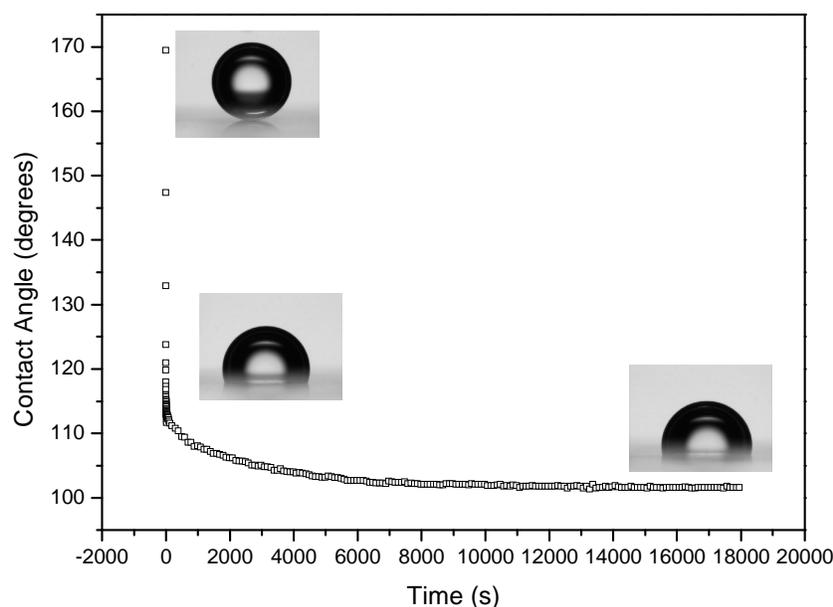
Figure 7. Spreading of a water drop on an acrylic plate, both immersed in mineral oil.

4. CONCLUSIONS

Experiments for each of the three systems were prepared, the spreading of the drops was recorded and a pos-processing analysis after the conclusion of the experiment was performed. For the water-oil-acrylic and oil-air-acrylic systems, the drop volume did not present any remarkable change in the course of the experiment. The static contact angle for these systems was obtained when there were no significant changes in the drop geometrical parameters. For the water-air-acrylic system, since the volume of the drop of water decreases due to its evaporation, the static contact angle was determined after the stabilization of the drop basis diameter.

The dynamics of spreading for non volatile liquids and partial wetting was also studied and a universal behavior for the characteristic function *H* was obtained, in good agreement with results found in the literature (Bracke et al., 1989).

5. ACKNOWLEDGEMENTS

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