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Precursor Film: A key driver to determine the wetting behavior in the vicinity of surface heterogeneity

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ABSTRACT

The experimental findings in recent past have clearly emphasized the role of three phase contact line in determining the wetting behavior of liquids. However, at microscopic level when the precursor film precedes the contact line, role of thin film on wetting behavior becomes important. Current study presents a series of simple experiments to establish the role of precursor films in controlling the wetting behavior in context of rising liquids in vertical planes. The experiments have been performed on glass capillaries and cover slips which have been modified partially hydrophobic by silanisation of some portion. Thus, two regions of significantly different

wetting behavior have been created. Experiments have been performed to capture the changes in wetting behavior as manifested by variation in capillary rise height and Wilhelmy force values, where hydrophilic and hydrophobic regions meet each other. The deviations in expected wetting behavior as the liquid approaches the boundary between two regions from hydrophilic end have demonstrated the role of precursor films on wetting behavior.

1. INTRODUCTION

Unlike ideal surfaces, real surfaces are rough and chemically heterogeneous in nature. Initial theoretical work by Wenzel[1] and Cassie-Baxter[2], introducing role of surface roughness and chemical heterogeneity, has been followed extensively to understand wetting on real solid surfaces[3-16]. These studies can be primarily classified into two categories- a) studies to understand the average wetting behavior of liquid drop in presence of multiple physical and chemical defects on surface[8-10] b) studies to understand the wetting behavior in close vicinity of a heterogeneous boundary or surface defect. The second category of studies has mainly addressed wetting in the context of position of contact line with respect to the heterogeneous boundary[11-14]. McCarthy[14] et al. have explained advancing and receding contact angles based on the position of a higher contact angle surface defect, outside and inside the contact line respectively and thereby the hysteresis. The pinning of contact line by particles has been suggested as one of three conditions for characteristic deposition of particles on periphery (coffee ring effect) of a droplet while it evaporates[15-16]. The experimental studies on single defect surfaces have clearly demonstrated that the interactions occurring in vicinity of three phase contact line control the apparent contact angles[17-18]. The recent article on modified capillaries by Extrand[19] et al. also highlights the fact of wetting line determining the contact angles rather than the interfacial areas involved. All above studies have been predominantly macroscopic and have investigated the phenomenon with respect to position of contact line. But at the microscopic level a nanoscale thin film known as precursor film, precedes the macroscopic droplet in the case of complete and partial wetting as explained by Popescu et al[20]. Therefore it is important to understand the encounter of thin film with surface defects and its effect on wetting behavior. Few studies in the past have demonstrated deviations in expected spreading behavior even before the contact lines encounter surface irregularities due to presence of precursor films[21-24]. The deposition studies by Edward Bormashenko[25] and Alexeyev et al.[26] have demonstrated the deposition of sodium chloride and silica particles respectively beyond three phase contact line. The experimental study by Lelah & Marmur[23] have shown that spreading rate of water droplet on a glass slide was affected by the edges of the solid surface and attributed it to interaction of precursor film with edges. It was observed that motion of primary (precursor) film front got arrested once it encountered the presence of edge which resulted in simultaneous thickening of precursor films. Since surface tension of a thin film depends on its thickness [30-32], the driving force for spreading of drop and rate of spreading were affected consequently. As the macroscopic investigations related to precursor films have been limited to spreading of sessile drops on horizontal planes, current study presents a series of experiments involving different geometries to bring new insights to it. The experiments have been conducted on thin capillaries and cover plates, immersed in water where water rises vertically over them.

2. EXPERIMENTS AND METHODS

The experiments have been performed on glass capillaries and cover slips separately. The capillaries and cover slips have been modified hydrophobic for some lengths by dip coating technique and thus creating two regions of dissimilar wetting behavior. The term boundary has been phrased for the meeting point of hydrophilic and hydrophobic regions.

2.1 MODIFYING GLASS CAPILLARIES AND COVER PLATES

Borosilicate glass capillaries having diameter 0.88 mm and length 100 mm were used in the study. The capillaries were washed with strong acid and alkali solution followed by rinsing with acetone and de-ionized water. The capillaries were rendered partially hydrophobic by clamping the dried capillaries and dipping in a silane **(Glass Coat from GE Toshiba Silicones Co. Ltd.)** solution for 2 hours to a particular length to render that length hydrophobic. The capillaries were kept in ambient condition for 8-10 hours for drying. Dried capillaries were rinsed and stored in de-ionized water to avoid any contamination, until they were used. The capillaries were made hydrophobic for three different lengths. The schematic of experimental set up is shown in **figure 1**. The glass cover slips were purchased from Blue Star having dimension 22 mm × 22 mm × 0.15 mm. The cover slips were rendered partially hydrophobic using the same method as mentioned for capillaries and stored in de-ionized water to avoid any contamination, until they were used.

2.2 MEASUREMENT METHODS

Water purified by Millipore Milli-Q system (1018Ω/cm) was used as probe liquid and was filled into a glass beaker. . All experiments were carried out at 25^0C. The measurement methods used for capillaries and cover slips are described in two separated sections:

2.2.1 CAPILLARIES

The schematic of experimental set up is shown in **figure 1**. A Magnifying lens was used to obtain magnified images of meniscus and to record the meniscus level. A CCD camera was connected to a computer to record the magnified images of the meniscus. A fiber optic cable connected to a light source and a lamp were used for illumination and locating the position of meniscus with precision. This assembly of lens and CCD camera was mounted on a vertical translation stage to locate and measure water level inside and outside of capillary. Two scenarios were considered, where in one case hydrophobic end was dipped first and in second case hydrophilic end was immersed first inside water. The objective was to capture the capillary rise behavior near boundary. All the height measurements for water level inside capillary were based on liquid level position inside capillary rather than the top of meniscus.

2.2.2 COVER SLIPS

Plate tensiometer technique was used to capture variation in wetting behavior near the hydrophilic-hydrophobic boundary by measuring the Wilhelmy Force values. For a thin plate like cover slips or platinum foil, in contact with a liquid, the net weight of the plate is given by the following equation:

$$W_{net} = W_{plate} + \gamma\, p \cos\theta - \delta v.\rho_l.g$$

Where γ is surface tension of liquid, p is perimeter and θ is contact angle made by the liquid meniscus with the plate. The second term in right hand side of equation refers to surface tension force exerted by meniscus (termed as Wilhelmy force[34]), while third term accounts for buoyancy. It is clearly evident from the equation that changes in contact angle values would be reflected by variation in net force values, measured by tensiometer. Therefore the intention was to capture the changes in Wilhelmy force values in vicinity of hydrophobic-hydrophilic boundary using plate tensiometer. The experiments were performed using KRUSS tensiometer (Model K-12). The cover slips were clamped vertically using the holder, provided with the tensiometer for measurements other than standard platinum plate. Water purified by Millipore Milli-Q system (1018Ω/cm) was used as probe liquid and was filled in glass container at bottom. The tensiometer was operated using the KRUSS software in contact angle mode to measure the net force experienced by the microbalance. Net force is considered to be a combination of buoyancy force and Wilhelmy force ($F_w = 2l\gamma\cos\theta$) as the instrument itself performs the base line correction to account for the weight of glass cover slip. The tensiometer program was set to measure net force at different immersed depths of cover-slips. The Wilhelmy force values were extracted by subtracting the buoyancy force from net force. As a sign convention, downward force has been considered as positive while upward force as negative. Again, experiments were performed for two different orientations of cover-slips. Again the experiments have been performed for two orientations of cover slips as similar to glass capillary section.

3. RESULTS AND DISCUSSION

3.1. CAPILLARIES

When the hydrophobic end was dipped first, the initial capillary rise behavior was similar to a typical hydrophobic capillary showing a constant negative capillary rise until meniscus hit the hydrophobic-hydrophilic boundary as shown in **figure 2**. A sudden change in water level inside the capillary was observed when meniscus touched the boundary. In addition the net capillary rise post the sudden increase in capillary rise (except the cases where the meniscus became closer to other end of capillary) was similar to a normal hydrophilic capillary. The phenomenon was found to be consistent for all three different coating lengths, irrespective of area fractions of hydrophobic and hydrophilic zones in contact with water as plotted in **figure 6**. This clearly demonstrated the role of contact line in determining the contact angles as suggested in single defect studies[17-19]. In another set of experiments, the hydrophilic end was initially dipped inside the beaker. Meniscus curvatures corresponding to each water level inside the capillaries were also recorded. The initial capillary rise was ~ 32 mm, which implied a contact angle of 12º and remained constant for some increased water levels inside the beaker as shown in **figure 3-a**. But as the water level inside capillary starting becoming closer to boundary, the difference between water levels inside and outside of capillary started to decrease **(figure 3-b and 3-c)** and became zero at the boundary as meniscus touched the boundary. Hereafter the water level inside capillary was less than the outside water level and showed rise behavior similar to a typical hydrophobic capillary **(figure 3-d and 3-e)**. The change in net capillary rise with respect to position of meniscus has been presented in **figure 7**. An important point to consider here is that predicted changes in the curvature and contact angle started happening even before meniscus touched the boundary of hydrophilic and hydrophobic part. This was in contrast with experiments where the hydrophobic end was immersed first. The explanation proposed is that the contact line of water was preceded by a thin film ("precursor Film") of nanometer scale thickness[27-29], which brought changes in wetting behavior as it approached the hydrophobic part as shown in **figure 4.** From **figure 7,** it is easy to read the transition length in which capillary height rise changes from a maximum positive value to zero. As the measurements of height were based on position of liquid level, therefore this length also included height of top of meniscus above liquid surface. The maximum height of meniscus was calculated as performed by Lane[35] taking into account of non-spherical curvature assumptions and comes around 0.442005543 mm. The average transition length from figure 4 comes around 3.11667 mm with standard deviation of 0.408575 mm. Hence the net transition length after taking accounting for meniscus height and standard deviations was equal to 2.708095 mm. This clarifies the doubt of transition length being given by the height of top of meniscus. In case of hydrophobic surface, the changes in wetting behavior happened at the boundary only. This can be related to absence of precursor films as has been suggested by George M. Whitesides[33] et al. in their experimental study on shapes of liquid fronts depending upon the liquid-surface interactions. The experiments were performed for three different coating lengths. In each case, the distance from boundary wherein the deviation from a standard capillary rise started happening, was recorded along with the meniscus images.

3.2. COVER SLIPS

The hydrophobic end of cover slips was dipped first inside water and net force was measured for different immersed depths. These net force values were used to extract Wilhelmy force by subtracting the buoyancy force. Initially being in contact with hydrophobic end (θ>90^0), cover slips felt a net upward force as depicted in **figure 5-a**. However, a sudden change was observed in net force values when it reached the boundary between hydrophobic-hydrophilic regions. The change was found to be repeatable at the same immersed depth. It is to be noted that this sudden change can be inferred as the sharpness of boundary. The net force value became positive after crossing the hydrophobic hydrophilic boundary because of water in contact with hydrophilic end. The extracted Wilhelmy force values are shown for three different coating lengths in **figure 8**. The phenomenon was found to be consistent for all coating lengths. In next set of experiments, the hydrophilic end was dipped first in water and net force values were recorded. Cover slips used for earlier measurements were used again. Initially being in contact with hydrophobic end (θ<90^0), cover slips felt a net downward force (positive) as depicted in **figure 5-b**. As from **figure 9**, Wilhelmy force values (which were positive) started decreasing on approaching close to the hydrophobic-hydrophilic boundary(similar to capillary experiments) and finally became zero at the boundary (similar to capillary experiments). After crossing the boundary the net force values started becoming negative and finally got saturated. Separately Wilhelmy force profiles for various dipping rates were also recorded as shown in **figure 10** and these showed the contrast with observations reported by Ghiradella et al.[36] where the transition lengths changed with variation in approaching velocities of contact line.

Above experiments have led to following key observations:

a) When the hydrophobic end was immersed in water, the wetting behavior followed that of a typical hydrophobic surface until the contact line hit the hydrophobic-hydrophilic boundary. After this the wetting behavior (Capillary rise and Wilhelmy Force) shown was similar to a typical hydrophilic surface.

b) When the hydrophilic end is immersed in water, the wetting behavior followed that of a typical hydrophilic surface until the contact line was a few millimeters away from the hydrophobic-hydrophilic boundary. The wetting behavior (Capillary rise and Wilhelmy Force) behavior showed deviation from a hydrophilic surface till it reached the boundary. The wetting behavior after crossing the boundary was like a typical hydrophobic surface.

The second observation is particularly interesting as there is a deviation from expected behavior even before the contact line reaches the boundary. We hypothesize that this is due to a thin precursor film which precedes the meniscus. As the precursor film approaches the heterogeneous boundary, the hydrophobic surface prevents further wetting of the film. Hence, the wetting behavior starts to deviate from a purely hydrophilic behavior. The changes in contact angle values before reaching the boundary could be explained by a similar argument as presented by Marmur et al.[2] The presence of heterogeneous boundary causes thickening of precursor film and consequently changes the surface tension values of film. The approach of investigating wetting behavior near surface irregularities has been instrumental in experimental design to demonstrate the macroscopic evidence of precursor films like in other studies[21-24].

4. CONCLUSION

The experiments with glass capillaries and cover plates imply that the precursor film moving ahead of contact line controls the wetting behavior. As a microscopic feature of moving bulk liquid, precursor film interacts first with surface than contact line and brings changes in contact angle values depending on the interaction. But, in absence of precursor films, the contact line solely dictates the wetting behavior. The arrest of precursor film at boundary of heterogeneity causes thickening and consecutive increase in contact angle values. The study presents a new macroscopic approach to infer the role the precursor film as a key driver influencing wetting behavior. The capture of contact angle values with the arrest of precursor film at the boundary is a highlighting feature of the study.

5. ACKNOWLEDGMENTS

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FIGURES

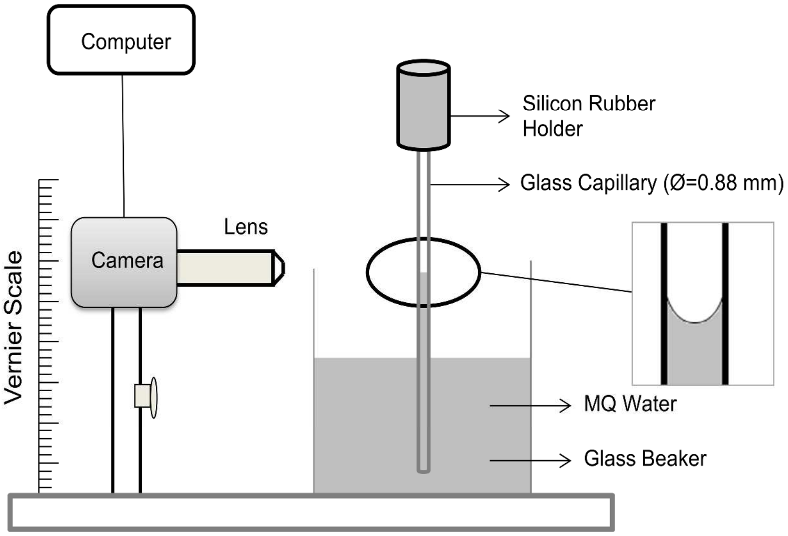


Figure 1: Experimental setup for studying capillary rise near the boundary of surface heterogeneity

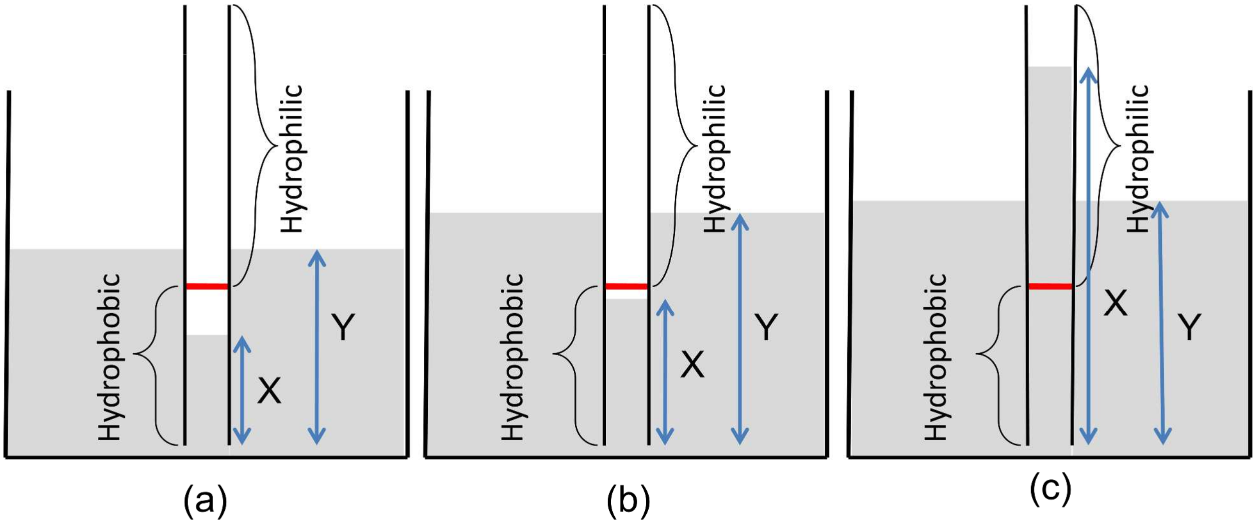


Figure 2: Series of observations as capillaries were immersed with hydrophobic end

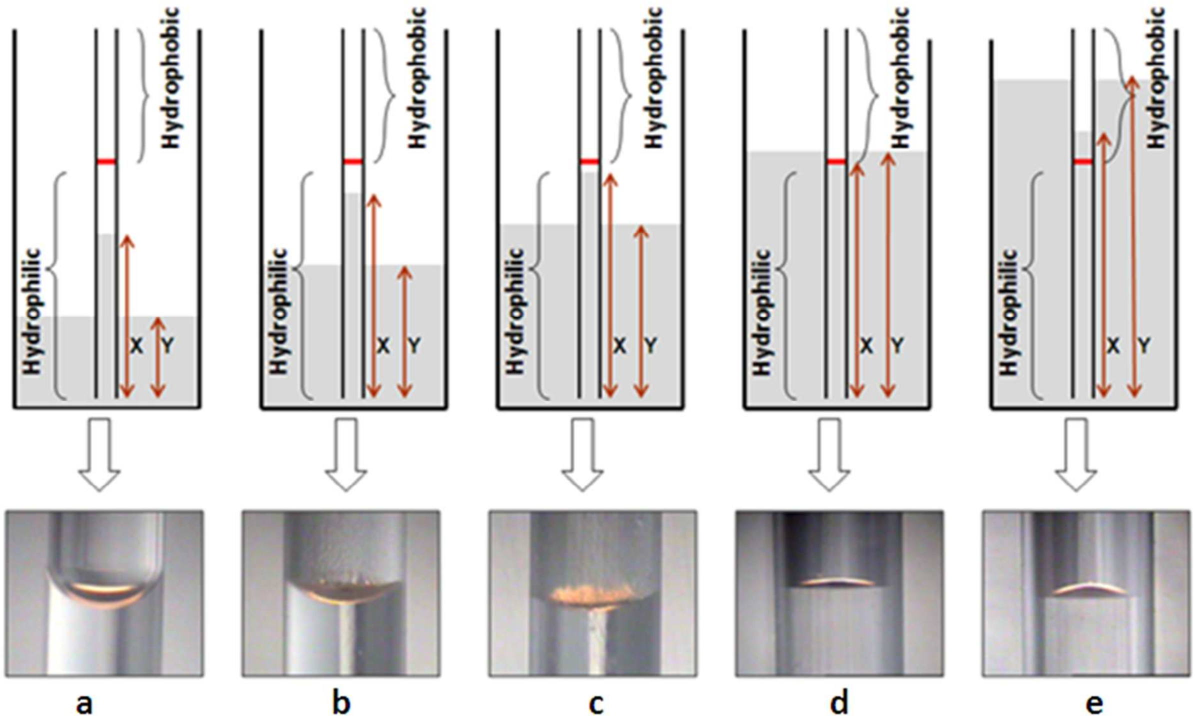


Figure 3: Series of observations along with meniscus images as capillaries were immersed with hydrophilic end

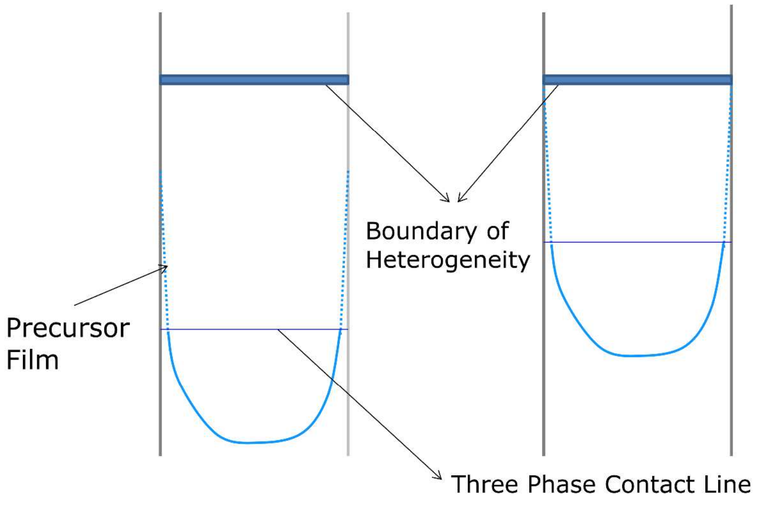


Figure 4: Schematic summary of observations: where the precursor film interacts much earlier than contact line with boundary of surface heterogeneity and changes the contact angle values

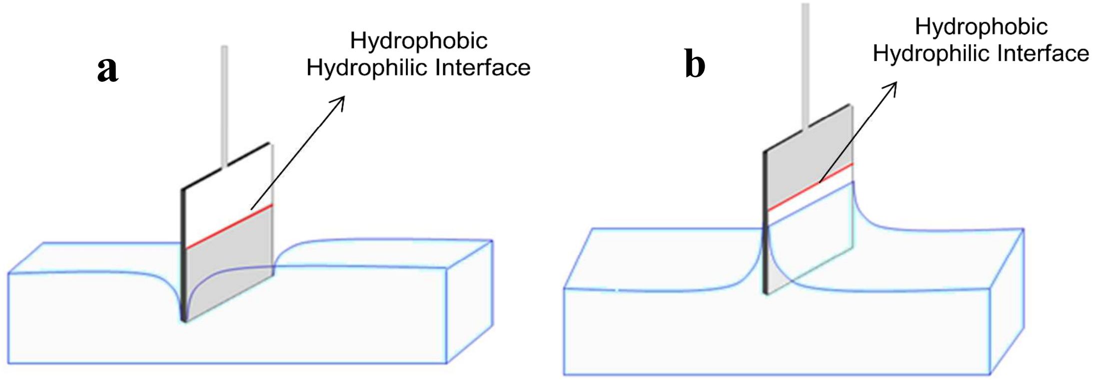


Figure 5: The drawing of Wilhelmy plate technique for observing the changes in contact angle values near the boundary of surface heterogeneity

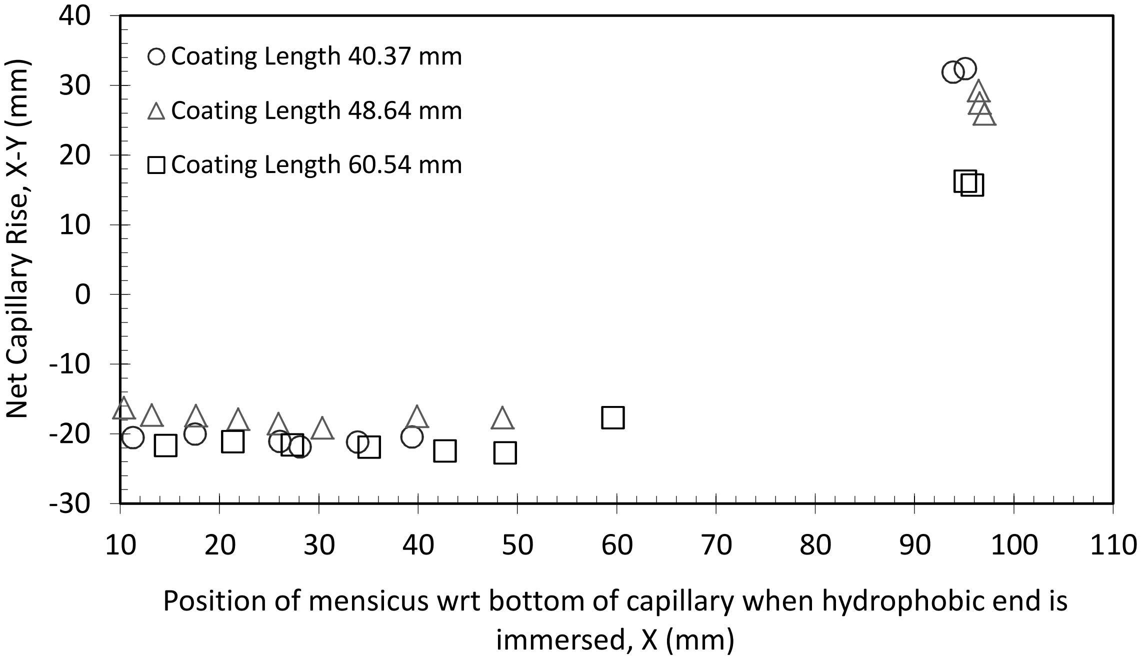


Figure 6: Net capillary rise vs. immersed depth when hydrophobic end of capillaries is immersed for three different silane coating lengths: a) 40.37 mm, b) 48.64 and c) 60.54 mm

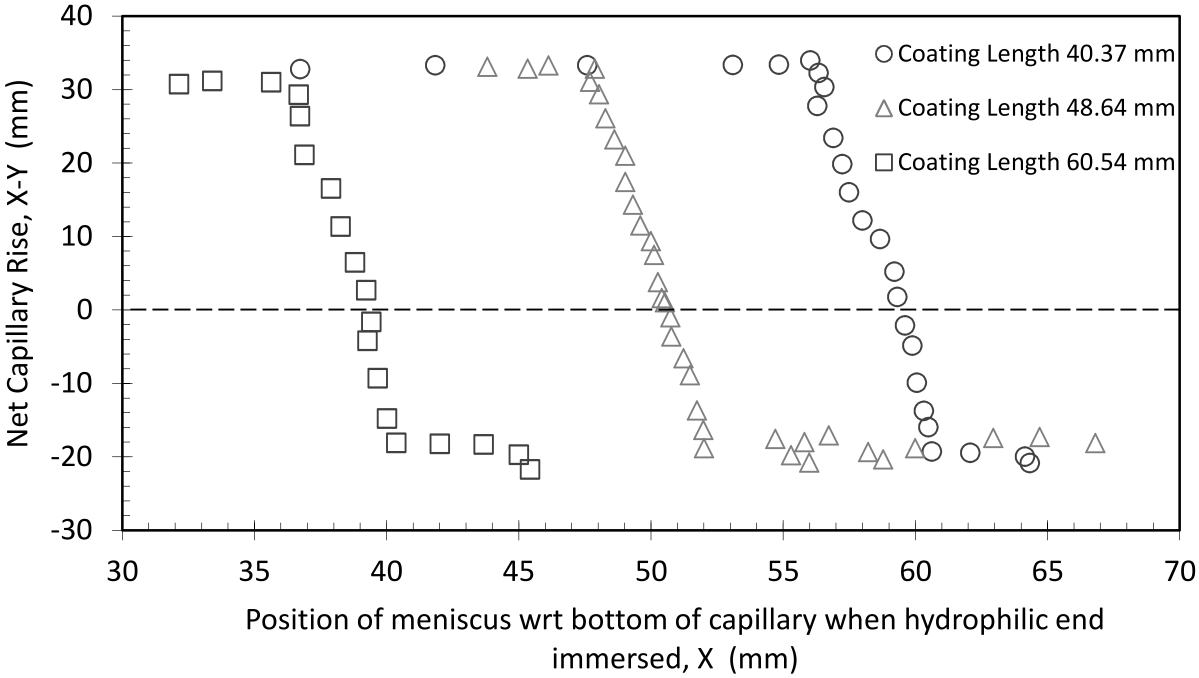
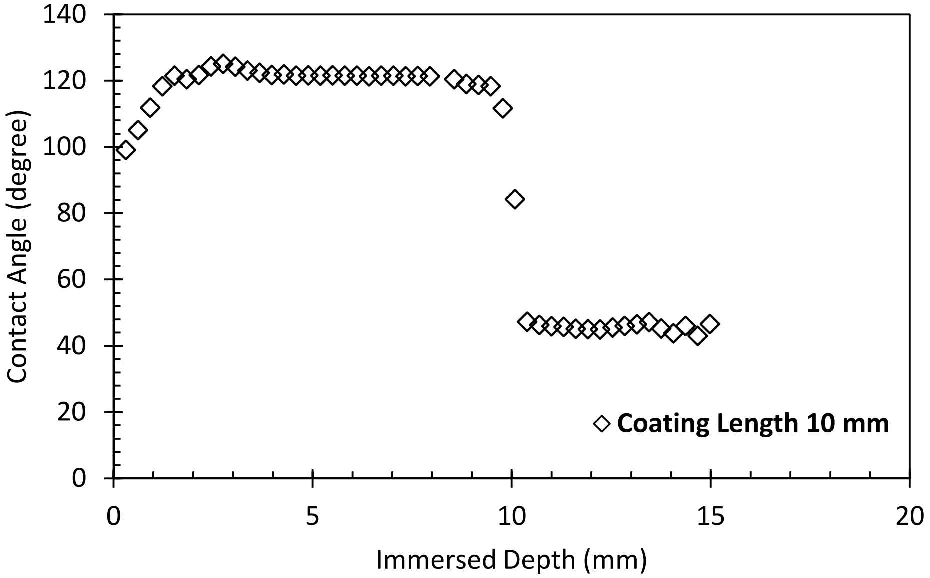
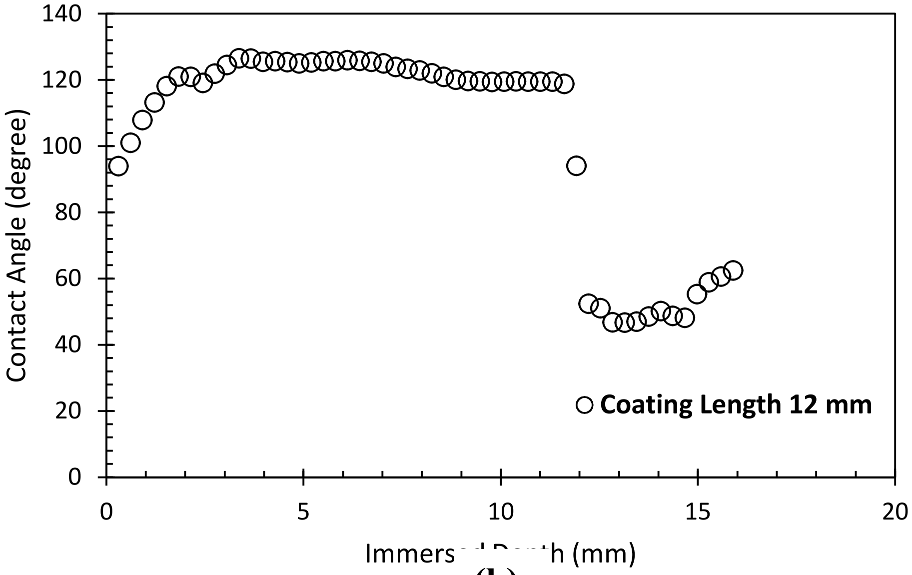


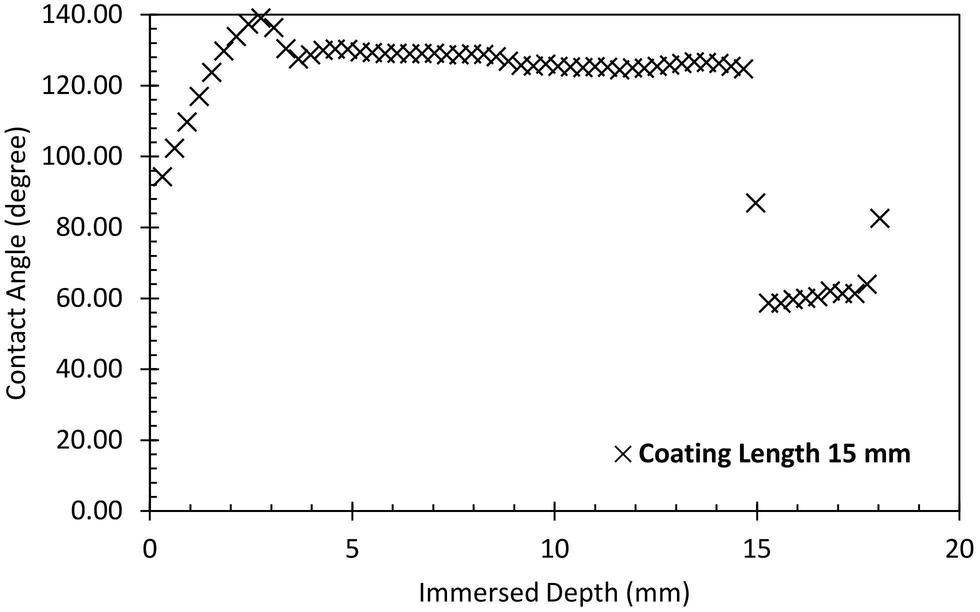
Figure 7: Net capillary rise vs. immersed depth when hydrophilic end of capillaries is immersed for three different silane coating lengths: a) 40.37 mm, b) 48.64 and c) 60.54 mm


140
120
100
80
60
40
20
0
Contact Angle (degree)
0
5
10
15
20
Immersed Depth (mm)
◇ Coating Length 10 mm

(a)

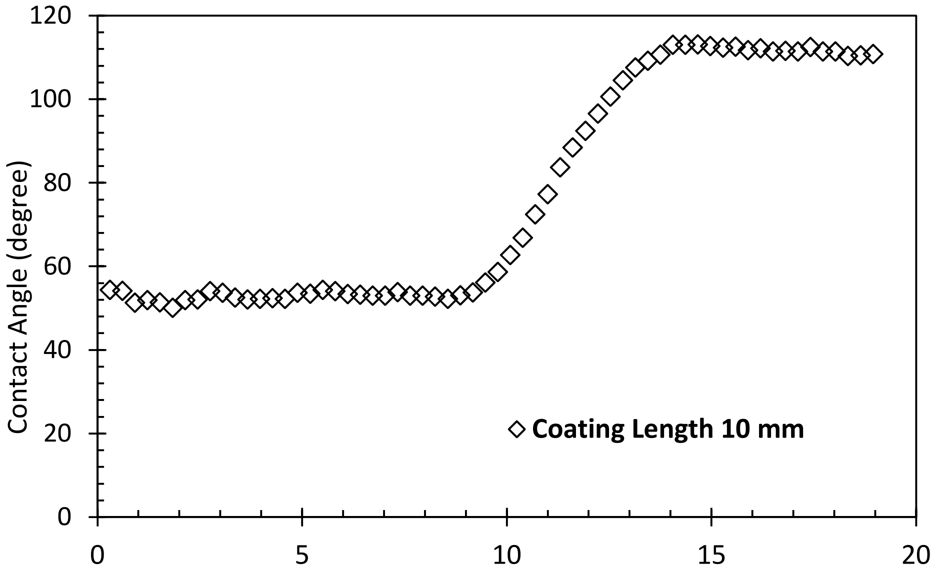

140
120
100
80
60
40
20
0
Contact Angle (degree)
0
5
10
15
20
Immersed Depth (mm)
○ Coating Length 12 mm

(b)

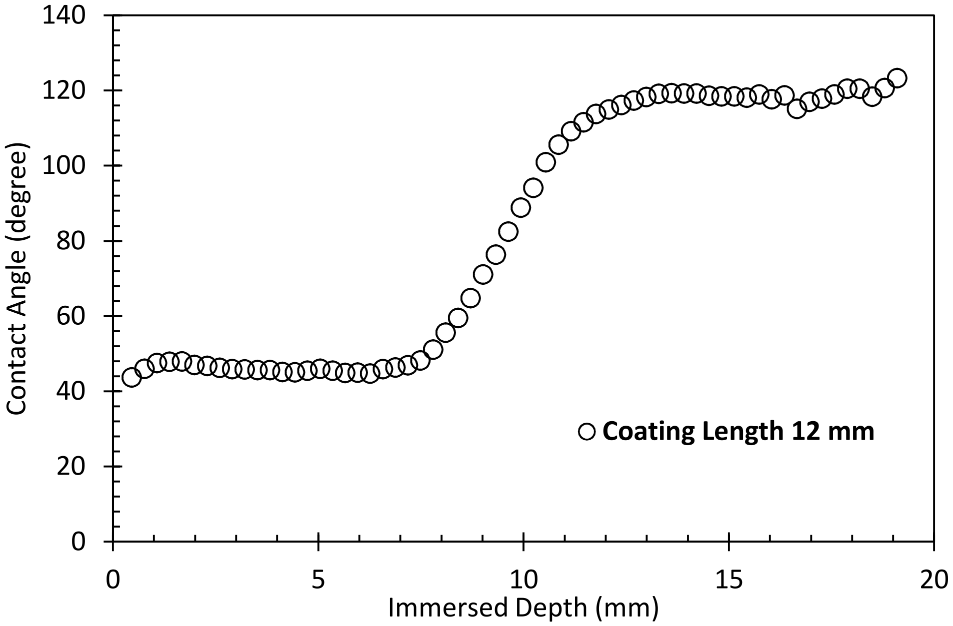


(c)

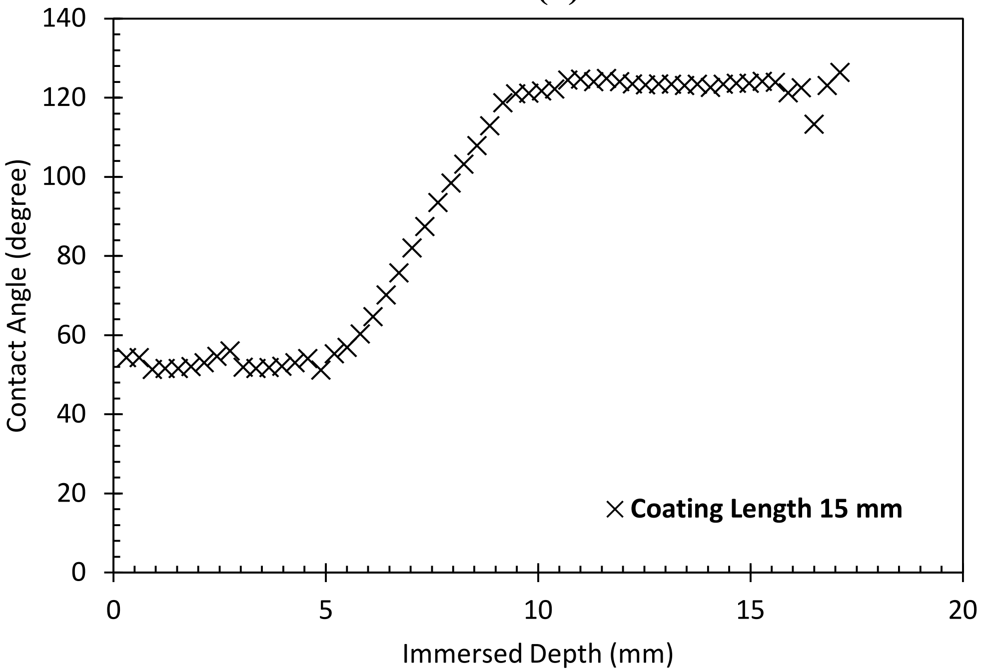
Figure 8: Wilhelmy force vs. immersed depth when hydrophobic end is immersed for three different silane coating lengths: a) 10 mm, b) 12mm & c) 15 mm



(a)



(b)



(c)

Figure 9: Wilhelmy force vs. Immersed Depth when hydrophilic end is immersed for three different silane coating lengths: a) 10 mm, b) 12mm & c) 15mm

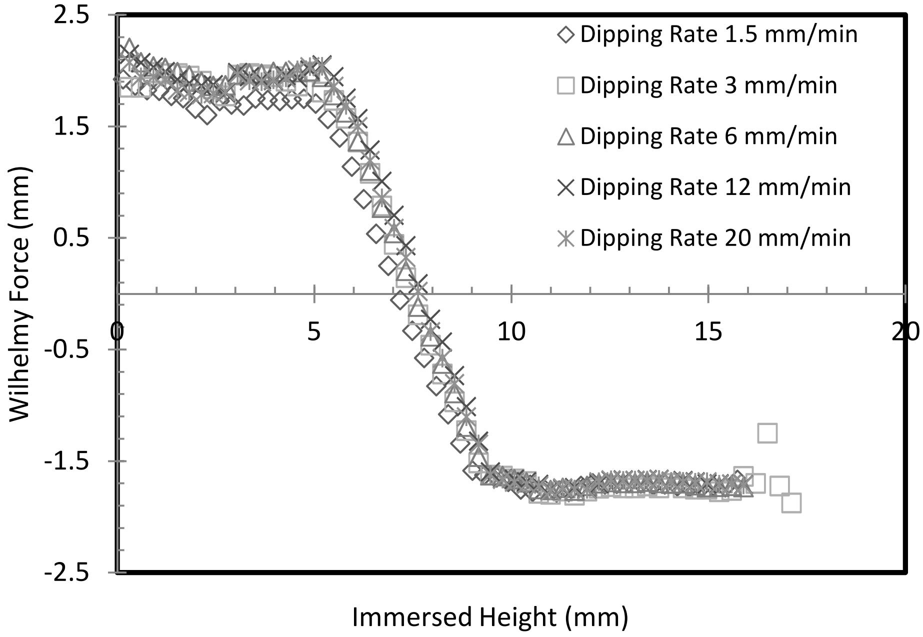


Figure 10: Wilhelmy force vs. immersed depth for various dipping rates as the hydrophilic end of cover slip is immersed

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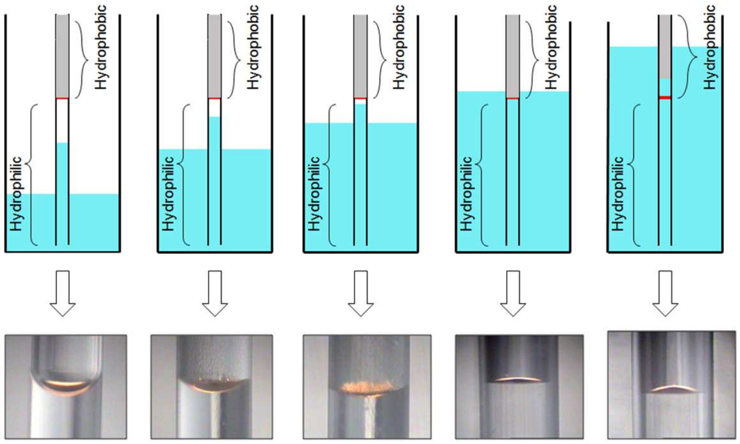

Multiple Water Meniscus Curvatures in Vicinity of Heterogeneous Boundary