



UNIVERSITY OF LEEDS

This is a repository copy of *Capillary Dynamics of Water/Ethanol Mixtures*.

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/92969/>

Version: Accepted Version

Article:

Cao, H, Amador, C, Jia, X et al. (1 more author) (2015) Capillary Dynamics of Water/Ethanol Mixtures. *Industrial and Engineering Chemistry Research*, 54 (48). pp. 12196-12203. ISSN 0888-5885

<https://doi.org/10.1021/acs.iecr.5b03366>

Reuse

Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Capillary dynamics of water/ethanol mixtures

Hui Cao^{1,}, Carlos Amador², Xiaodong Jia³ and Yulong Ding¹*

¹School of Chemical Engineering, University of Birmingham, B15 2TT, United Kingdom

²Procter & Gamble Newcastle Innovation Center, Newcastle Upon Tyne, NE12 9TS, United Kingdom

³School of Chemical and Process Engineering, University of Leeds, LS2 9JT, United Kingdom

Corresponding Author*h.cao@bham.ac.uk

ABSTRACT Surface tension and contact angle play important roles in capillary dynamics during washing commission of spray-dried detergent powder where interaction between surface chemistry and liquid is concerned. An experimental study for the dynamics of water/ethanol mixtures in both hydrophilic and hydrophobic capillary tubes has been investigated. The combination of water/ethanol mixtures and Trimethylchlorosilane coating on capillaries provides a variety of liquid surface tension and contact angle for the penetrating system. Significant differences of penetrating speed on hydrophilic and hydrophobic tubes indicate that dynamic contact angle dominates hydrophobic surface while liquid surface tension plays a more important role on hydrophilic surface. The speed gradient of different liquids on hydrophilic surface is greater than hydrophobic surface, mainly due to the domination between hydrogen bonding

structures and water polarity while liquid moves on surfaces covered with different chemistry, physically absorbed water on silica capillaries or silanol groups covered capillaries.

KEYWORDS Capillary dynamics; Silylation; Hydrophilic; Hydrophobic; AFM

1. INTRODUCTION

Porous media can be characterized by studying the kinetics of liquid rise within the pore spaces¹. The penetration of liquids into porous materials due to capillary action is important in a wide range of technological fields such as agriculture, oil recovery, pharmaceuticals, chemical engineering and civil engineering²⁻⁴. A porous medium is a complicated system of connected pores, and in most of the case these pores have rough walls and throats which makes the study of capillary mechanism critically relevant. The kinetics of the penetration in these pores is considered to be influenced mainly by its structure (pore geometry, surface roughness etc.) and the wettability of the constituent pores. However, due to scale and imaging limits, investigation of flow kinetics in these random porous medium is very difficult at pore-level. Instead, using glass micromodels and capillary tubes can simplify this study while providing informative parameters which are difficult to probe directly in these naturally random porous medium.

Kinetics of liquid rise in single capillary tubes was formulated almost at the same time by Lucas⁵, Washburn⁶, and Rideal⁷ in the early 20th century. Assuming contact angle of fluid meniscus during displacement was constant, Washburn derived fluid flow equation in capillary tubes using Poiseuille's law⁶ and suggested that penetrating length is proportional to root time. Quere reported an linear relationship during early stages of rise by experiment⁸ and observed oscillations around the equilibrium stages when the liquid viscosity is low enough⁹. The author

along with other researchers^{1, 10-11} proved that dynamic contact angle should be implemented in Washburn's equation in order to make a better agreement between experimental data and equation predictions. Hence, an intensive collection of dynamic contact angle in different capillary system is essential for scientists to improve the theoretical prediction.

Spray-dried detergent powder normally is considered as random porous medium. Due to process differences and formulation divergences, the surface chemistry of spray-dried detergent powders has a variety wetting properties to water. From industrial application's point of view, it is imperative that investigation of water penetrating into these porous medium during washing commission and understanding how capillary dynamics influence the performance of detergent powder to be carried out. A detailed investigation of the action between the surface chemistry of capillary and liquid molecular regarding the capillary flow dynamics is of more interesting to researchers. There have been several experimental investigations on the effects of velocity and capillary number on dynamic contact angle, and empirical correlations have been developed since then¹²⁻¹⁶. Not until very recently, an extensive, well-characterized experimental study of dynamic contact angle changes with meniscus velocity in capillary rise experiments for different fluid systems has been reported¹⁷. However these works have very limited information of statistic experimental data sets especially for liquids with different surface tension and contact angle in capillaries where surface chemistry is concerned. Few researchers reported capillary kinetics of liquid penetrating into different surfaces without concerning contact angle changes. An earlier paper focused on penetration rate, wetting force and surface free energy changes when water/ethanol mixtures penetrating into silanized silica fibrous assemblies by measuring electrical conductivity¹⁸. But their results lack information of mixture penetration behaviour and the relatively parameters to guide the development of predictive models. Bain reported

penetration kinetics of surfactant solution on hydrophobic capillaries assuming dynamic contact angle is equal to equilibrium contact angle¹⁹. Starov²⁰ presented a theoretical model trying to link contact angle with aqueous surfactant solution where contact angle is always bigger than 90°. To the best of our knowledge, there are very limited number of experimental data sets available in the literature that can be used to characterize the variation of dynamic contact angle in a system where surface chemistry on the capillary tube has been concerned. Therefore, the extent and quality of the experimental data on this interfacial parameter are highly desirable for the predictive capabilities of the models that one can develop and potentially in the future to predict capillary actions on detergent powder during washing commissions.

In the present study, penetration rates of water/ethanol mixtures into hydrophilic and hydrophobic capillary tubes have been investigated considering different surface tension and contact angle effects. Glass tubes were treated with silane coupling agents to modify the surface chemistry of the capillary first. Then Atomic Force Microscope (AFM) was used to observe surface structure changes before and after silane treatment. The advancing meniscus of liquid was recorded by high speed camera and videos were analysed by ImageJ to extract the penetration height as a function of time. Detailed discussion about the action between hydroxyl groups (OH) on capillary surface and inside liquid has been presented regarding the capillary flow dynamics. Dynamic contact angle changes in both hydrophilic and hydrophobic capillaries was plotted based on the calculation from empirical equations.

2. EXPERIMENT

2.1. Materials

Capillaries. Capillaries with three different inner radius purchased from World Precision Instruments Ltd were used in the experiments, 0.34 mm, 0.45 mm and 0.56 mm. Before experiment, the capillaries were first embedded in pure ethanol and ultrasonicated for half an hour to remove the remains. Then they were flushed by deionised water, rinsed in deionised water and ultrasonicated for another half an hour. At last, they were dried in clean air atmosphere at 60°C for 12 hours. Hydrophobic capillaries were obtained by exposing clean capillaries to Trimethylchlorosilane (Sigma-Aldrich, purity > 99%) for 12 hours at room temperature, which then reacted with the silanol groups on glass tube surface. The capillaries were stored at 20°C separately in desiccators with silica gel and were exposed to 20°C and 65% relative humidity prior to use.

Chemicals. Deionised water and pure ethanol were mixed with different ratio as showing in **Table 1**.

2.2. Methods

Capillary dynamics. The capillary rise dynamics was followed from the moment when capillary tube contacted the liquid and stopped when liquid meniscus balanced at certain height. First, liquid was placed in a cylindrical glass dish filled slightly over the rim to allow imaging immediately when the capillary tube touched the liquid. Fast rise processes were recorded by a high speed camera (FASTCAM SA 5, Photron Ltd) connected to a computer. The camera was set up at 2000 frames per second. The images were analysed by software ImageJ. The schematic was shown in **Figure 1**.

Surface morphology. The inner surfaces of capillaries before and after coating process were scanned by AFM in order to investigate the effect of coating process on surface morphology.

Physical properties. Physical properties of the liquids were measured, including density, viscosity and surface tension, by a Density Meter (DMA Generation M, Anton Paar), a Rheometer (MCR Series, Anton Paar) and a Contact Angle Measuring System (EasyDrop, KRUSS), respectively. Results are listed in **Table 1**.

3. RESULTS AND DISCUSSION

3.1. Atomic morphological studies

Wettability of a solid surface to a certain liquid is governed by two factors, i.e. a chemical factor and a geometrical factor of the surface²¹⁻²³. Barthlott and Neinhuis first reported that both surface microstructure and chemical composition of a solid surface can determine its hydrophobicity²⁴. Later on, researchers further studied by finely controlling the micro/nanostructure or chemical composition of a surface, the contact angle of water on this surface can be manipulated between hydrophilic and hydrophobic²⁵⁻²⁸.

Silylation is a popular process to change a hydrophilic surface into hydrophobic property²⁵. In this study, we coated TMCS on capillary tubes to change the surface chemistry. **Figure 2** and **Figure 3** are typical AFM images of the unmodified and TMCS modified glass tube inner surface, respectively. The images were recorded at 2 μm planar in contact mode. **Figure 2** (a) and **Figure 3** (a) are two dimensional (2D) images, and **Figure 2** (b) and **Figure 3** (b) are three dimensional (3D) images. In 2D images, **Figure 3** (a) shows slightly bigger dot features comparing to **Figure 2** (a). And in 3D images, these peak features in **Figure 3** (b) are rougher than **Figure 2** (b) which indicates a higher surface roughness. The root-mean-square (RMS) roughness values of the films analysed by AFM show that the surface roughness of TMCS modified glass tube is twice as the unmodified one, with a RMS roughness value of 7.8

nm and 15.1 nm, respectively. AFM results show that the process of TMCS coating on glass tube surface does change the surface topography in a considerable level. Surface roughness has a influence on both the contact angle itself and its hysteresis. An important aspect is the length scale involved. For roughness significantly below the wavelength of light, which is the case here, the effect of surface roughness can be described by the so-called Wenzel equation²⁹. The equation predicts that if a molecularly hydrophobic surface is rough, the appearance is that of an even more hydrophobic surface. If a hydrophilic surface is roughened it becomes more hydrophilic²⁹. The coating layer on capillary surface nearly doubles the roughness, which from the morphology point of view should enhance the hydrophilicity. However, since the silanol groups are hydrophobic, capillary tubes become hydrophobic consequently.

3.2. Fundamental equations of capillary dynamics

As applied to a viscous noncompressible liquid in a long cylindrical capillary, the Newton dynamics equation can be expressed as³⁰

$$\rho[hh'' + (h')^2] = \frac{2}{r}\gamma \cos \theta - \frac{8}{r^2}\mu hh' - \rho gh, \quad (1)$$

where ρ is the density (kg/m^3), μ is the viscosity ($\text{Pa}\cdot\text{s}$), γ is the surface tension (N/m), θ is the contact angle of the liquid ($^\circ$), h is the height of capillary rise (m), r is the capillary radius (m), and g is the standard gravity (m/s^2). The equation assumes the Poiseuille flow profile throughout the capillary. The capillary liquid will rise to an equilibrium level, h_{eq} , established by the balance of gravity and capillarity³¹

$$h_{eq} = \frac{2\gamma \cos \theta_{eq}}{\rho gr}, \quad (2)$$

where θ_{eq} is the equilibrium contact angle. By measuring the equilibrium height of each penetration through the video of high speed camera, using Eq. (2), θ_{eq} can be calculated.

A simplified equation derived from Eq. (1), gives the rate of liquid penetration into a perpendicular capillary as follows⁵⁻⁶:

$$h = \sqrt{\frac{\gamma r}{2\mu} \cos \theta t}, \quad (3)$$

in which the height of capillary rise $h \sim t^{1/2}$. This is the famous Lucas-Washburn equation. It is well known that in this equation, some terms for example the gravity effects, the kinetic effects, the viscous loss in liquid below the tube, and the viscous loss associated with the entrance effects, have been neglected³². A more detail report showed that capillary rise of low viscosity liquid in a vertical tube can be characterized into three regimes: i) pure acceleration regime, $h \sim t^2$, ii) linear regime, $h \sim t$, and iii) Washburn regime, $h \sim t^{1/2}$,^{16-17, 27}. Moreover, as mentioned previously, the contact angle in Eq. (3) should be dynamic contact angle.

3.3. Experimental results of capillary penetration

Capillary tubes with three inner radius of 0.34 mm, 0.45 mm and 0.56 mm were used to perform the experiments while liquids in **Table 1** were assisted. **Figure 4** shows images captured by high speed camera. The movement of meniscus were clearly captured by the experiment set up in **Figure 1**. After using ImageJ to analyse all the videos, **Figure 5** and **Figure 6** show the penetration height verses penetration time which is plotted as log 10 in order to magnify the differences. **Figure 5** is hydrophilic surface and **Figure 6** is hydrophobic surface. Obviously, three regimes are detected throughout capillary tube sizes for both hydrophilic and hydrophobic surface, which is very similar to literature¹⁷. Besides, water does not rise up to hydrophobic

capillary tube at all suggesting that the contact angle for water on TMCS modified surface is greater than 90° . Meanwhile, ethanol and ethanol/water mixture can still go into hydrophobic tubes.

By comparing **Figure 5** and **Figure 6**, it is clear that flow dynamics in hydrophilic tubes is different from hydrophobic tubes. For hydrophilic ones, with more ethanol in the liquid, the equilibrium time and height h_{eq} , and penetration speed all decrease. While in hydrophobic ones, it is the opposite. With increasing ethanol ratio in the liquid, equilibrium height h_{eq} and penetration speed increase explicitly, and slightly for the penetration time.

The equilibrium height as a function of ethanol volume ratio in water is plotted in **Figure 7**. On hydrophobic capillary, low volume ethanol mixtures have lower equilibrium height than high volume ethanol mixtures which is in the opposite direction of hydrophilic capillary. In hydrophilic surface, with increasing ethanol content in mixtures, the equilibrium height reduces 61%, 61% and 64% on 0.34 mm, 0.45 mm and 0.56 mm capillary tube respectively. In hydrophobic surface, while ethanol volume increase from 20% to 100%, the equilibrium height on 0.34 mm, 0.45 mm and 0.56 mm capillaries increases 159%, 140% and 170% respectively. From **Table 1**, it is clear that surface tension of the liquid reduces nearly 70% from water to ethanol, which is nearly the deduction of equilibrium height in hydrophilic capillaries, implying that surface tension governs in hydrophilic capillary dynamics. While in hydrophobic capillary, as surface tension decreases from 20% to 100% of ethanol volume in liquid, the equilibrium height increase drastically. By taking the two aspects, i.e. liquid surface tension and contact angle, it is likely that a large drop in contact angle occurred from 20% ethanol to 100% ethanol in hydrophobic capillaries.

It is also seen that throughout the experiment, some oscillation occurred around the equilibrium status. This phenomenon was reported and studied by researchers before^{1, 9, 30}. It was shown that kinetic force is the main reason that may cause the oscillation of liquid column. As liquid rises up in capillary, viscous force damps the oscillatory energy out, which leads to an oscillatory behaviour at the liquid front around the equilibrium height (also called Jurin height)⁹. The critical radius, R_{cr} , can be determined by³²:

$$R_{cr} = 2 \left[\frac{\mu^2 \gamma \cos \theta_{eq}}{\rho^3 g^2} \right]^{\frac{1}{5}}. \quad (4)$$

The equation indicates if $R > R_{cr}$, the kinetic force is strong enough to rise liquid up the equilibrium height, which leads to oscillation around Jurin height. According to Eq. (4), the value of critical radius R_{cr} in silica capillaries, for water is 0.47 mm, for ethanol is 0.45 mm, and for the mixtures are between 0.56 mm and 0.63 mm. In **Figure 5** (a) where capillary radius is 0.34 mm, no oscillation was observed around the equilibrium height. In **Figure 5** (b) while capillary radius is 0.45 mm, a very invisible oscillation occurred on ethanol which can be neglected. However in **Figure 5** (c) while capillary radius is 0.56 mm, a slightly visible oscillation happened around the Jurin height for both water and ethanol. Similar phenomena happened again in hydrophobic capillaries.

3.4. Advancing contact angle

Researchers have proposed that during capillary rise process, the contact angle θ in Eq. (1) changes significantly before the meniscus stabilize, which could dominate the process^{10, 31, 33}. Consequently, dynamic contact angle θ_{ad} should be used in Eq. (1) instead of constant value or equilibrium contact angle for any model prediction. Predicting results of Eq. (1) using

equilibrium contact angle are compared to experiment results in 0.34 mm radius tube for both hydrophilic and hydrophobic surfaces, showing in **Figure 8**. On both hydrophilic and hydrophobic capillaries, predicting results show higher penetrating speed than experiment result. Dynamic contact angle on most surfaces exhibits hysteresis, i.e. the advancing and receding contact angles are different. For the capillary rising case, advancing contact angle plays important role and should be used in Eq. (1)³⁴.

The dynamic contact angle is dependent on the velocity of the moving meniscus, or capillary number. Over the last several decades, researchers have introduced various semi empirical correlations to describe the velocity-dependence of dynamic contact angle¹²⁻¹⁵. A proposed accurate empirical correlation is given by^{13, 16}

$$\cos \theta_{ad} = \cos \theta_{eq} - 2(1 + \cos \theta_{eq})Ca^{1/2}, \quad (5)$$

where $Ca = \frac{\mu}{\gamma} v$ is the capillary number, and v is the velocity of contact line which can be calculated by derivating the rise-versus-time curves in **Figure 5** and **Figure 6**. The calculated advancing contact angle is plotted against capillary number as showing in **Figure 9**.

The general distribution of advancing contact angle in hydrophilic tubes is quite different from hydrophobic tubes. **Figure 9** (a) shows the variation of advancing contact angle with capillary number for displacement of air by different liquid in hydrophilic tubes with 0.34mm, 0.45mm and 0.56mm inner radius. The results are very comparable to the direct image measuring data reported by Heshmati and Piri¹⁷. **Figure 9** (b) shows the variation of advancing contact angle in hydrophobic tubes. It is clearly shown that for the same liquid, advancing contact angles in three different sized tubes have very similar distribution. As indicated in Eq. (5), advancing contact

angle is mainly related to equilibrium contact angle and capillary number. For different sized capillary tubes, especially those used in this study, the equilibrium heights are similar in most of the cases except for pure water in hydrophilic tubes (see **Figure 7**), which result in similar equilibrium contact angles (Eq. (2)). Hence, advancing contact angles for the same liquid in different sized capillaries share similar values across capillary numbers.

However, for different liquid, advancing contact angle shows strong relevant to capillary number in hydrophilic system, and gradually less relevant with decreasing ethanol volume ratio in liquid in hydrophobic capillaries. It is also noticeable that ethanol volume ratio in hydrophilic surface has much less effect on contact angle comparing to hydrophobic surface. With more water in the liquid, advancing contact angle varies from 20° to nearly 80° at low capillary number area. This is probably due to the silanol groups of TMCS coating on capillary surface make it very water repellent. The advancing contact angle results confirmed our previous suspect that in the hydrophilic surface, liquid surface tension dominates the flow dynamics, while in the hydrophobic surface, advancing contact angle plays a more important role in the flow dynamics. It is noteworthy that the advancing contact angle for a given capillary number shows, weak sensitivity to the type of fluid system in a hydrophilic surface. While in the hydrophobic surface, strong relevant has been observed. This may have important implications for development of modelling tools used to predict flow at the pore scale in porous media.

3.5. Wettability of hydrophilic and hydrophobic capillaries

In **Figure 10**, the wetting force in the advancing scan, $\gamma \cos \theta_{ad}$, is plotted against the volume ratio of ethanol in the liquid at time $t = 0$ s which is the initial stage of capillary penetrating on hydrophilic and hydrophobic surfaces while tube radius is 0.34 mm. The value of $\gamma \cos \theta_{ad}$

decreased with increasing ethanol concentration for the unmodified capillary tube, and increased for TMCS modified capillary tube, which is consistent with the literature¹⁸. Especially on hydrophilic surface, with additive of ethanol in liquid, wetting force decreases drastically comparing to pure water. Such a result is more significant by comparing the hydrophilic penetrating behaviour to the hydrophobic results in **Figure 5** and **Figure 6**. The difference of penetration speed for different ethanol/water mixtures of the hydrophobic one is much greater than the hydrophilic one. This is probably caused by the silanol groups on the hydrophobic surface.

Studies shows that a layer of physically absorbed water molecular presents on the surface of silicates and silicas³⁵⁻³⁶ and makes them hydrophilic initially. After being coated by TMCS, a layer of hydrophobic TMCS was formed on the tube surface and nearly doubled the surface roughness, as illustrated by AFM results in **Figure 2** and **Figure 3**. Different chemistries on capillaries surfaces cause different penetrating behaviour. For the case of pure water in the unmodified capillary, water can easily form hydrogen bond to the physically absorbed water on the silica surface and rise up in the tube continuously until equilibrium. On TMCS coated surface, it is difficult for water to form any bond to TMCS functional groups. Besides, water is a highly polar molecule, and TMCS is an organic material with low polarity. As a result water does not rise up in the tube.

Each sp^3 hybridized oxygen atom can form four approximately tetrahedrally disposed hydrogen bonds in liquid water³⁷. Similar to water, ethanol can be regarded as having a sp^3 hybridized tetrahedral oxygen³⁸. Since the oxygen atom of an ethanol molecule carries one proton and two lone pairs of electrons, it might form three hydrogen bonds with its neighbors - another ethanol molecule or a water molecule³⁸. As a result, water and ethanol can form different hydrogen-

bonding structures. For the case of pure ethanol in unmodified capillaries, similar to water, ethanol can rise up in the tube by forming hydrogen bonds with the pre-absorbed water on the tube surface. For the case of pure ethanol in TMCS modified capillaries, due to its less polarity and same organic group (CH₃) to TMCS, ethanol can also rise up in the tube. The results in **Figure 10** show that ethanol has very similar wetting force on both silica and TMCS coated capillaries, hence very similar penetration behaviour.

The case of water/ethanol mixtures is more complicated. As discussed above, water and ethanol can mix freely by forming different hydrogen bonds between each other. When increasing ethanol concentration in the mixtures, especially after 40 vol%, since ethanol is statistically twice as likely to act as a proton acceptor than as a donor, ethanol is more dominant than water in the mixture³⁸. Consequently, wetting forces of different water/ethanol mixtures on both silica and TMCS coated capillaries are eventually close to the value of pure ethanol. One exceptional case is ethanol at 20 vol %. On both hydrophilic and hydrophobic tubes, wetting force is either significantly higher or smaller than pure ethanol which gives indication that in this mixture, the polarity of water still plays an important role comparing to the hydrogen bond structures.

4. CONCLUSIONS

Although identified 200 years ago, wetting still lives and bounces constantly thanks to new questions—often arising from practical consideration. The dynamics of water/ethanol mixtures in both silica capillary tubes and silylated silica capillary tubes has been investigated with various tube radius by high speed camera at 2000 frames per second. The AFM results indicate that the silylation process on silica capillary tubes nearly doubles the surface roughness while surface chemistry has been change (from hydrophilic surface to hydrophobic surface) which also

been proved by the capillary penetration results. The gradient of penetrating speed for different water/ethanol volume ratio is greater on the TMCS treated capillaries than silica capillaries. Dynamic contact angle calculated from empirical equation based on penetrating results show that in hydrophilic surface, liquid surface tension dominate capillary rise, while in hydrophobic surface, contact angle plays a more important role. Drastic drop of wetting force with additive of ethanol in liquid explained that domination between hydrogen bonding structures and water polarity is the key reason for different penetration behaviour in the system.

ACKNOWLEDGMENT

The authors would like to give their acknowledgement to Procter & Gamble Ltd., Newcastle Technical Centre for the research support.

REFERENCES

- (1) Hamraoui, A.; Nylander, T., Analytical Approach for the Lucas–Washburn Equation. *Journal of Colloid and Interface Science* **2002**,*250* (2), 415.
- (2) Babadagli, T., Dynamics of Capillary Imbibition When Surfactant, Polymer, and Hot Water Are Used as Aqueous Phase for Oil Recovery. *Journal of Colloid and Interface Science* **2002**,*246* (1), 203.
- (3) Saguy, I. S.; Marabi, A.; Wallach, R., Liquid imbibition during rehydration of dry porous foods. *Innovative Food Science & Emerging Technologies* **2005**,*6* (1), 37.
- (4) Brielles, N.; Chantraine, F.; Viana, M.; Chulia, D.; Branlard, P.; Rubinstenn, G.; Lequeux, F.; Lasseux, D.; Birot, M.; Roux, D.; Mondain-Monval, O., Imbibition and Dissolution of a Porous Medium. *Industrial & Engineering Chemistry Research* **2007**,*46* (17), 5785.
- (5) Lucas, R., Ueber das Zeitgesetz des kapillaren Aufstiegs von Flüssigkeiten. *Kolloid-Zeitschrift* **1918**,*23* (1), 15.
- (6) Washburn, E. W., The Dynamics of Capillary Flow. *Physical Review* **1921**,*17* (3), 273.
- (7) Rideal, E. K., CVIII. On the flow of liquids under capillary pressure. *Philosophical Magazine Series 6* **1922**,*44* (264), 1152.
- (8) Quéré, D., Inertial capillarity. *EPL (Europhysics Letters)* **1997**,*39* (5), 533.
- (9) Quéré, D.; Raphaël, E.; Ollitrault, J.-Y., Rebounds in a Capillary Tube. *Langmuir* **1999**,*15* (10), 3679.
- (10) Siebold, A.; Nardin, M.; Schultz, J.; Walliser, A.; Oppliger, M., Effect of dynamic contact angle on capillary rise phenomena. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2000**,*161* (1), 81.
- (11) Mumley, T. E.; Radke, C. J.; Williams, M. C., Kinetics of liquid/liquid capillary rise. *Journal of Colloid and Interface Science* **1986**,*109* (2), 398.

- (12) Cox, R. G., The dynamics of the spreading of liquids on a solid surface. Part 1. Viscous flow. *Journal of Fluid Mechanics* **1986**,168, 169.
- (13) Joos, P.; Van Remoortere, P.; Bracke, M., The kinetics of wetting in a capillary. *Journal of Colloid and Interface Science* **1990**,136 (1), 189.
- (14) Shikhmurzaev, Y. D., The moving contact line on a smooth solid surface. *International Journal of Multiphase Flow* **1993**,19 (4), 589.
- (15) Sheng, P.; Zhou, M., Immiscible-fluid displacement: Contact-line dynamics and the velocity-dependent capillary pressure. *Physical Review A* **1992**,45 (8), 5694.
- (16) Bracke, M.; De Voeght, F.; Joos, P., The kinetics of wetting: the dynamic contact angle. In *Trends in Colloid and Interface Science III*, Bothorel, P.; Dufourc, E. J., Eds. Steinkopff: 1989; Vol. 79, pp 142.
- (17) Heshmati, M.; Piri, M., Experimental Investigation of Dynamic Contact Angle and Capillary Rise in Tubes with Circular and Noncircular Cross Sections. *Langmuir* **2014**,30 (47), 14151.
- (18) Tagawa, M.; Gotoh, K.; Nakagawa, Y., Penetration of water/ethanol mixtures into silanized silica fibrous assemblies. *Journal of Adhesion Science and Technology* **1998**,12 (12), 1341.
- (19) Bain, C. D., Penetration of surfactant solutions into hydrophobic capillaries. *Physical Chemistry Chemical Physics* **2005**,7 (16), 3048.
- (20) Starov, V. M., Spontaneous rise of surfactant solutions into vertical hydrophobic capillaries. *Journal of Colloid and Interface Science* **2004**,270 (1), 180.
- (21) Onda, T.; Shibuichi, S.; Satoh, N.; Tsujii, K., Super-Water-Repellent Fractal Surfaces. *Langmuir* **1996**,12 (9), 2125.
- (22) Lathe, S. S.; Nadargi, D. Y.; Venkateswara Rao, A., TMOS based water repellent silica thin films by co-precursor method using TMES as a hydrophobic agent. *Applied Surface Science* **2009**,255 (6), 3600.
- (23) Sanjay, S. L.; Hirashima, H.; Rao, A. V., TEOS based water repellent silica films obtained by a co-precursor sol-gel method. *Smart Materials and Structures* **2009**,18 (9), 095017.
- (24) Barthlott, W.; Neinhuis, C., Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **1997**,202 (1), 1.
- (25) Rao, A. V.; Lathe, S. S.; Dhere, S. L.; Pawar, S. S.; Imai, H.; Ganesan, V.; Gupta, S. C.; Wagh, P. B., Control on wetting properties of spin-deposited silica films by surface silylation method. *Applied Surface Science* **2010**,256 (7), 2115.
- (26) Jin, M.; Feng, X.; Feng, L.; Sun, T.; Zhai, J.; Li, T.; Jiang, L., Superhydrophobic Aligned Polystyrene Nanotube Films with High Adhesive Force. *Advanced Materials* **2005**,17 (16), 1977.
- (27) Zhao, M.-H.; Chen, X.-P.; Wang, Q., Wetting failure of hydrophilic surfaces promoted by surface roughness. *Scientific Reports* **2014**,4, 5376.
- (28) Bico, J.; Marzolin, C.; Quéré, D., Pearl drops. *EPL (Europhysics Letters)* **1999**,47 (2), 220.
- (29) Wenzel, R. N., RESISTANCE OF SOLID SURFACES TO WETTING BY WATER. *Industrial & Engineering Chemistry* **1936**,28 (8), 988.
- (30) Zhmud, B. V.; Tiberg, F.; Hallstenson, K., Dynamics of Capillary Rise. *Journal of Colloid and Interface Science* **2000**,228 (2), 263.
- (31) Xue, H. T.; Fang, Z. N.; Yang, Y.; Huang, J. P.; Zhou, L. W., Contact angle determined by spontaneous dynamic capillary rises with hydrostatic effects: Experiment and theory. *Chemical Physics Letters* **2006**,432 (1-3), 326.

- (32) Masoodi, R.; Languri, E.; Ostadhossein, A., Dynamics of liquid rise in a vertical capillary tube. *Journal of Colloid and Interface Science* **2013**,389 (1), 268.
- (33) O'Loughlin, M.; Wilk, K.; Priest, C.; Ralston, J.; Popescu, M. N., Capillary rise dynamics of aqueous glycerol solutions in glass capillaries: A critical examination of the Washburn equation. *Journal of Colloid and Interface Science* **2013**,411, 257.
- (34) Imanishi, K.; Einaga, Y., Effects of Hydrophilic Chain Length on the Characteristics of the Micelles of Pentaoxyethylene n-Decyl C10E5 and Hexaoxyethylene n-Decyl C10E6 Ethers. *The Journal of Physical Chemistry B* **2005**,109 (15), 7574.
- (35) Zhuravlev, L. T., The surface chemistry of amorphous silica. Zhuravlev model. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2000**,173 (1–3), 1.
- (36) Hair, M. L., Glass Surfaces Hydroxyl groups on silica surface. *Journal of Non-Crystalline Solids* **1975**,19, 299.
- (37) Frank, H. S.; Wen, W.-Y., Ion-solvent interaction. Structural aspects of ion-solvent interaction in aqueous solutions: a suggested picture of water structure. *Discussions of the Faraday Society* **1957**,24 (0), 133.
- (38) Franks, F.; Ives, D. J. G., The structural properties of alcohol-water mixtures. *Quarterly Reviews, Chemical Society* **1966**,20 (1), 1.

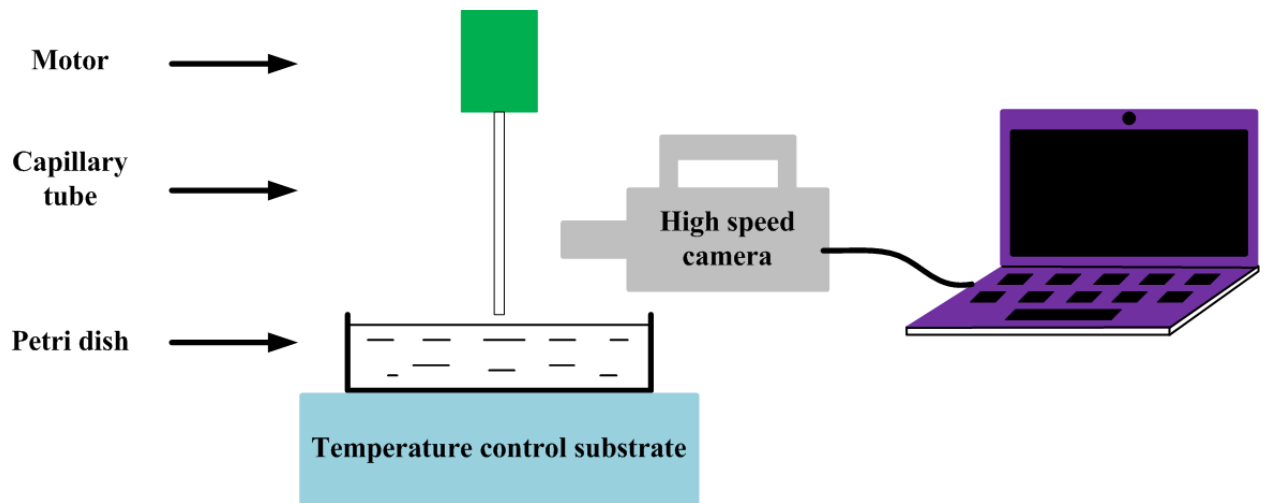
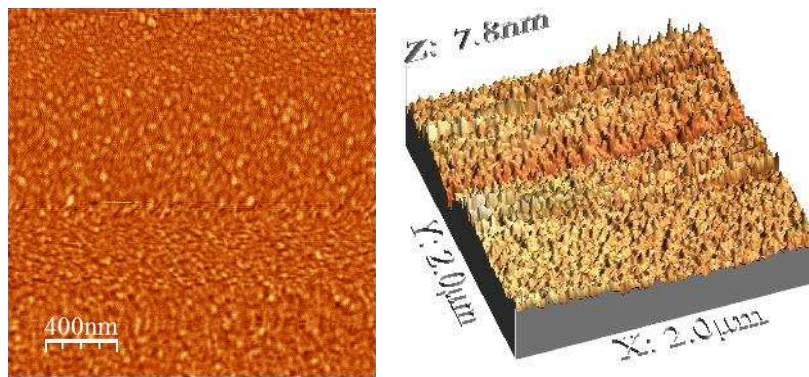


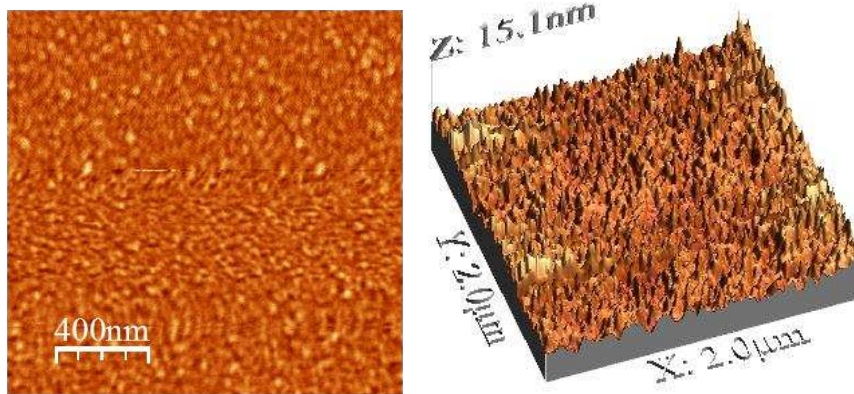
Figure 1. Schematic of experiment set up.



(a)

(b)

Figure 2. AFM tomographic image of unmodified capillary tube surface (hydrophilic one).



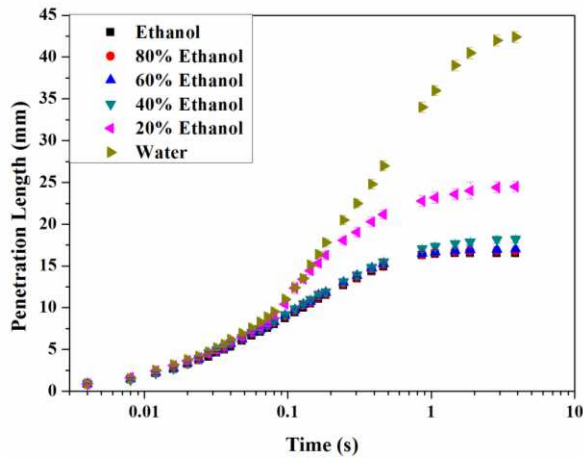
(a)

(b)

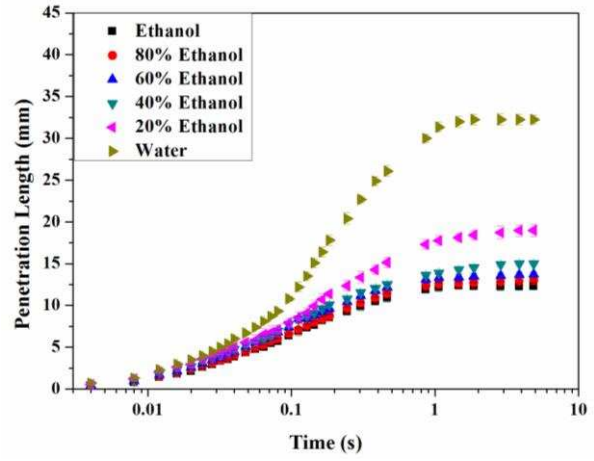
Figure 3. AFM tomographic image of TMCS modified capillary tube surface (hydrophobic one).



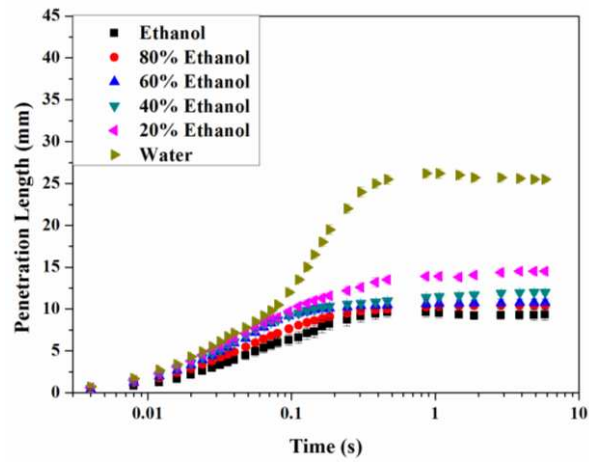
Figure 4. Images captured from high speed camera video show the motion of liquid meniscus in capillary tube.



(a)

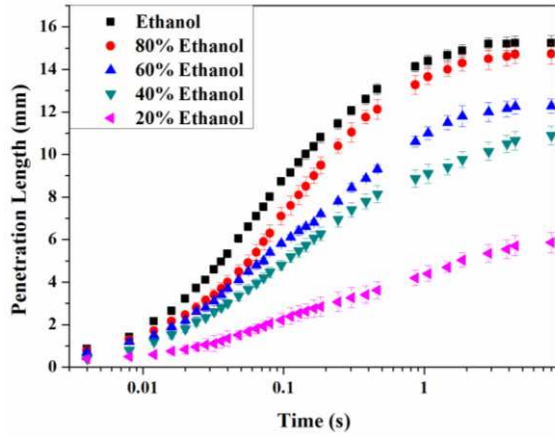


(b)

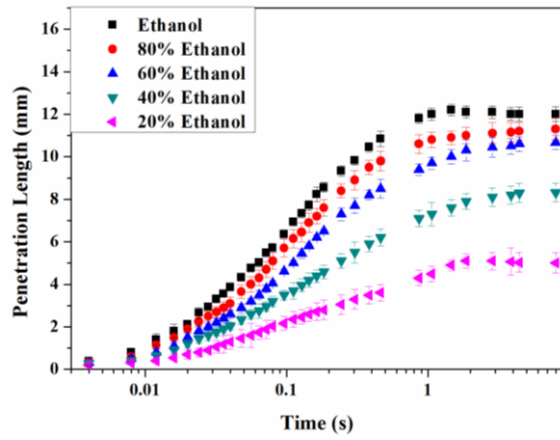


(c)

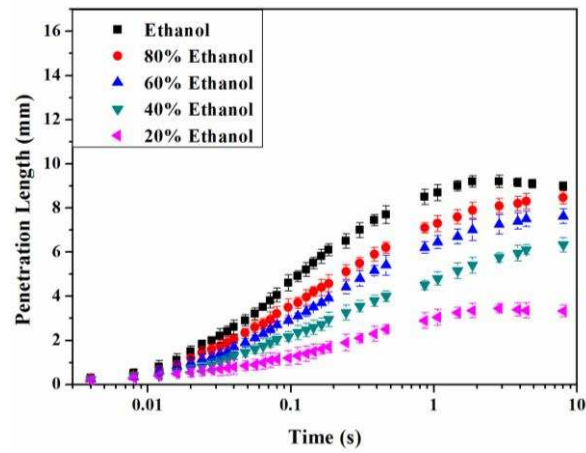
Figure 5. Experimental results of liquids penetrating into hydrophilic capillary glass tube for radius of 0.34 mm (a), 0.45 mm (b), and 0.56 mm (c).



(a)



(b)



(c)

Figure 6. Experimental results of liquids penetrating into hydrophobic capillary glass tube for radius of 0.34 mm (a), 0.45 mm (b), and 0.56 mm (c).

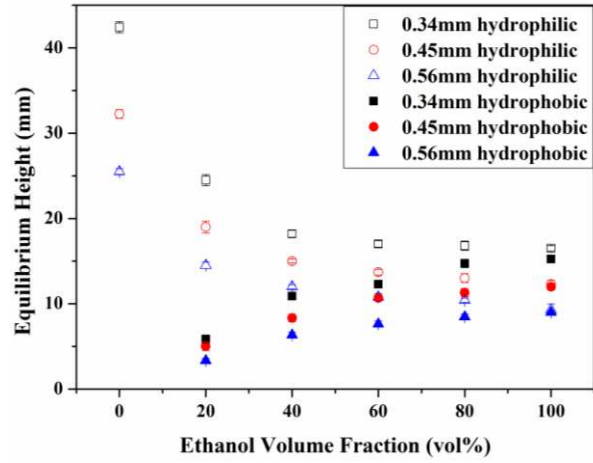
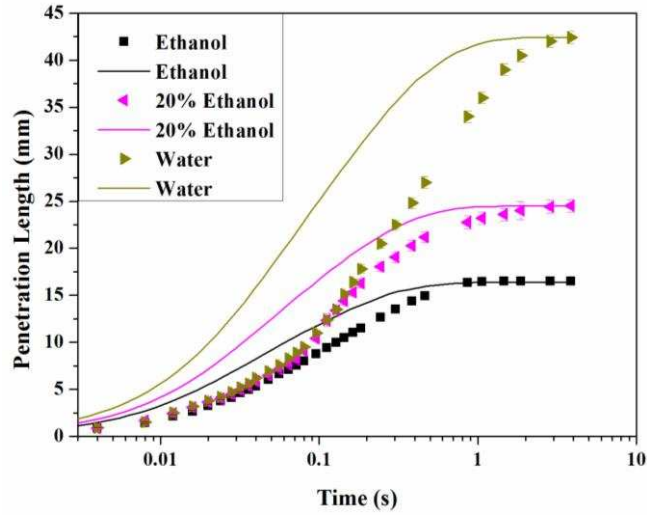
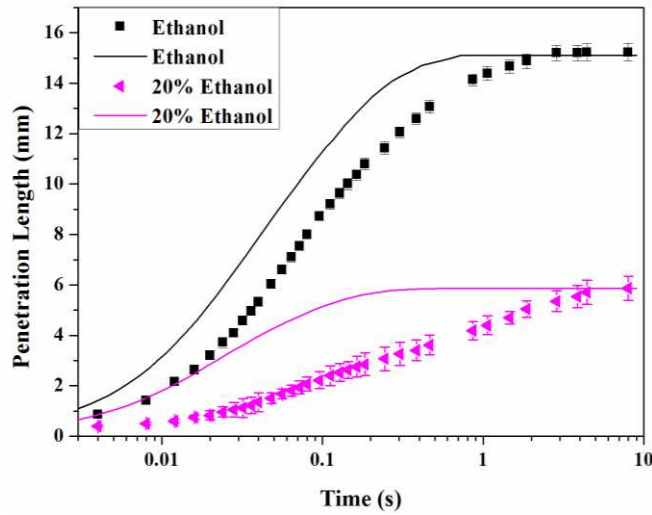


Figure 7. Equilibrium height as a function of ethanol volume ratio on hydrophilic and hydrophobic surface. Solid dots are hydrophilic capillary tube, and open dots are hydrophobic capillary tube.

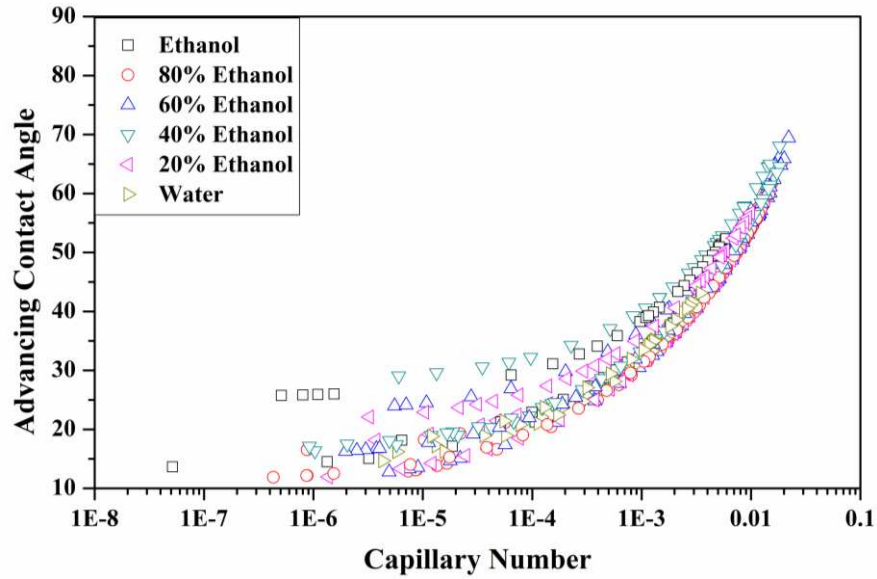


(a)

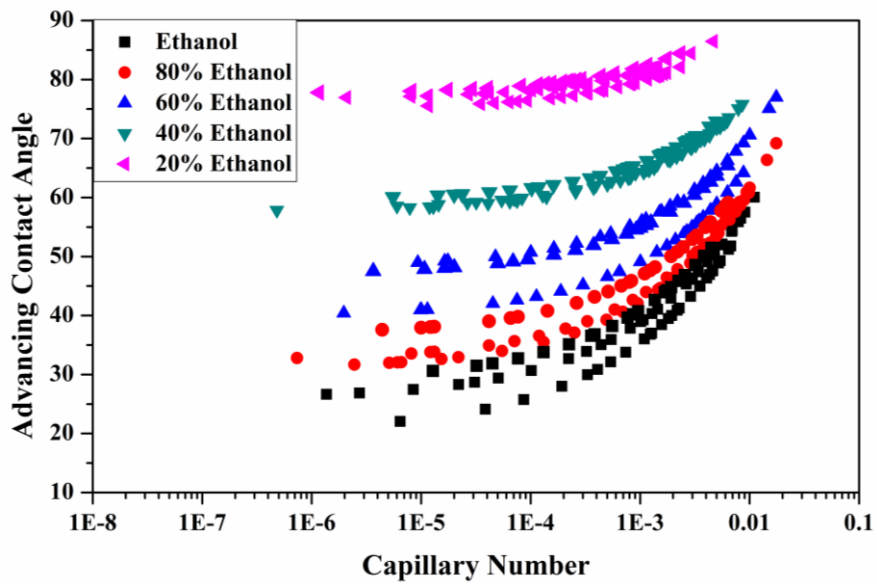


(b)

Figure 8. Comparing penetrating experiment results with Eq. (1) calculation using equilibrium contact angle in (a) hydrophilic capillaries and (b) hydrophobic capillaries when tube size is 0.34 mm in radius.



(a)



(b)

Figure 9. Variation of dynamic contact angle vs capillary number for different water/ethanol liquid in three size glass tube 0.34 mm, 0.45 mm, and 0.56 mm for (a) hydrophilic and (b) hydrophobic.

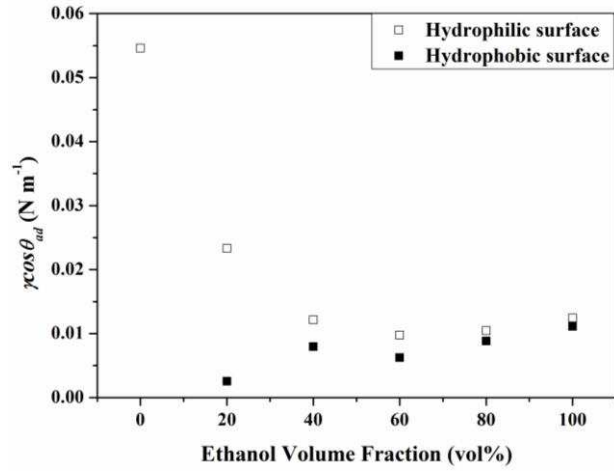


Figure 10. Wetting force as a function of the ethanol volume ratio in liquid on hydrophilic and hydrophobic surfaces at time $t = 0$ s when tube radius is 0.34 mm.

Table 1. Physical properties measuring results of water/ethanol mixtures by volume fraction at 20°C in atmosphere.

		80% Water	60% Water	40% Water	20% Water	
Liquid	Water	& 20%	& 40%	& 60%	& 80%	Ethanol
		Ethanol	Ethanol	Ethanol	Ethanol	
Density						
$\rho(10^3 \text{ kg/m}^3)$	0.9982	0.9733	0.9460	0.9043	0.8551	0.7884
Viscosity μ						
$(10^{-3} \text{ Pa}\cdot\text{s})$	1.002	1.9316	2.7917	2.7855	2.1807	1.144
Surface						
tension γ	72.75	41.48	32.47	27.76	24.87	22.27
(10^{-3} N/m)						