Conference paper

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**Water–surface interactions and definitions for hydrophilicity, hydrophobicity and superhydrophobicity**

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Abstract: Hydrophilicity and hydrophobicity are among the most important concepts in surface chemistry. Samuel and co-workers reported the measure of interactive forces between water and 20 different surfaces using the microbalance technique. Results showed that the wetting force correlates well to the advancing contact angle ($\theta_A$), the larger the $\theta_A$ the lower the surface wettability. The adhesion force, measured when the water and surface first separates, correlates well to the receding contact angle ($\theta_R$), the larger the $\theta_R$ the smaller the surface adhesion. The data also reveals that small residual water droplets are observed after the water droplet and the surface separate for surfaces with $\theta_R < 90^\circ$. This indicates high water affinity for these surfaces. No residual water droplet is observed for surfaces with $\theta_R > 90^\circ$. From the basic meaning of philicity-phobicity, $\theta_R \sim 90^\circ$ is proposed as the new cut-off between hydrophilicity and hydrophobicity. The main driver for hydrophobicity is attributed to the high water surface tension. The merit of this proposed definition is discussed. Since wetting interaction becomes zero at $\theta_A \geq 145^\circ$, surfaces with $\theta_R > 90^\circ$ and $\theta_A \geq 145^\circ$ can further be defined as superhydrophobic. The extension of this approach to define oleophilicity/phobicity and superoleophobicity with hexadecane is discussed.

Keywords: adhesion; chemistry education; contact angle; hydrophilicity; hydrophobicity; NICE-2014; oleophobicity; superhydrophobicity; surface chemistry; surface properties; wettability.

Introduction

The study of surfaces is a very important branch of science that touches all facets of our lives. Understanding how a surface and liquid interact is of tremendous value to many seemingly unrelated applications, such as painting, coating, window washing, lawn care, lubrication, liquid transportation in microfluidic devices, anti-icing surfaces on roof-tops and airplanes, anti-fouling surfaces in ships, printing particularly inkjet printing in printed electronic device manufacturing, etc. Static and dynamic contact angle measurements are commonly used to study surface wettability, adhesion and other related processes, such as wetting, spreading and de-wetting. Figure 1 depicts the schematic for the determination of static contact angle $\theta$, advancing contact angle $\theta_A$ and receding contact angle $\theta_R$. Experimentally, $\theta$ is determined by first depositing a liquid droplet (~5 μL) from a micro syringe gently onto a horizontal flat solid surface. After the liquid droplet reaches its static steady state and the image of the droplet was captured by a camera in a
goniometer. The tangential angle resulting from the balance of the surface tensions among the solid–vapor, liquid–vapor and solid–liquid interface is the Young’s angle of contact \([1]\), commonly known as the static contact angle \(\theta\). Advancing and receding contact angles \(\theta_A\) and \(\theta_R\) are determined by the drop expansion/contraction method. Specifically, \(\theta_A\) is the angle measured when the sessile droplet is expanding, from \(\sim 2\) to \(20\) \(\mu\)L, for example, by adding a small volume of a liquid \((0.15\ \mu\)L/s) continuously to the sessile droplet. Receding contact angle \(\theta_R\) is determined by withdrawing a small volume of the liquid from the expanded sessile droplet.

Hydrophobicity and hydrophilicity are among the most important concepts in surface science. In Greek words, hydro means water, philicity means affinity and phobicity means lack of affinity. In the scientific community, researchers generally accept that a surface is hydrophobic when its static water contact angle \(\theta\) is \(>90\)° and is hydrophilic when \(\theta\) is \(<90\)°. There is little technical rationalization or understanding why a surface suddenly becomes hydrophobic when \(\theta\) just increases \(1\)° from the cut-off point. What is the mechanism or molecular origin that leads to this change of surface property? In fact, this definition has recently been questioned by Gao and McCarthy who called “Teflon hydrophilic” because of its high adhesion with water \([2]\). Others have also noticed this shortfall in the definition. Van Oss \([3]\) proposed to use the free energy of hydration \((\Delta G_{sl})\) as the measure of hydrophilicity and hydrophobicity. Based on the analysis of the free energy of hydration \((\Delta G_{sl})\) for a number of compounds, he found that hydrophobic compounds attract each other in water when \(\Delta G_{sl} > -113\ \text{mJ/m}^2\); and that they repel each other when \(\Delta G_{sl} < -113\ \text{mJ/m}^2\). The value \(-113\ \text{mJ/m}^2\) was proposed to be the cut-off between hydrophobicity and hydrophilicity. Vogler \([4]\) proposed a cut-off of \(\theta \sim 65\)° based on the appearance and disappearance of long range hydrophobic interactions. These two definitions actually have little to do with water–surface affinity. Rather, the cut-off point shows the raise of the hydrophobic effect of surfactant molecules in water. In this paper, an improved definition for hydrophilicity and hydrophobicity is proposed. Surfaces with \(\theta_R < 90\)° are shown to have definite affinities toward water and they are defined as hydrophilic. Surfaces that display lack of affinity with water are hydrophobic and their \(\theta_R\) is \(>90\)°. The underlying mechanism for hydrophobicity is discussed. Moreover, a surface is defined as superhydrophobic when its \(\theta_R\) is \(>90\)° and \(\theta_A\) is \(\geq 145\)°. No measurable attraction between water and a superhydrophobic surface is evident. The extension of this methodology to define oleophilicity/oleophobicity and superoleophobicity for hexadecane is discussed.

Water–surface interactions and contact angle measurements

Earlier, Samuel et al. \([5]\) launched a systematic study to find out what surface properties contact angle measurements are actually measuring. The result is briefly outlined as the following. Using a highly sensitive microbalance in a tensiometer, these authors measured both wetting (attractive) and adhesion forces between a water droplet and a variety of surfaces \((1–20)\). These surfaces represent surfaces of all traits, from hydrophilic to hydrophobic to superhydrophobic based on the common accepted definitions. A schematic of the water–surface interaction experiment is given in Fig. 2 and details of the procedures and analysis have been published elsewhere \([5, 6]\).
Experimentally, a 5 mg water droplet was first deposited onto a platinum ring, which is attached to a microbalance. The surface of interest is placed on a stage where it can move up-and-down steadily at a slow rate (10 μm/s) by a computer-controlled stepping motor. Prior to the measurement, the microbalance is set at zero. When the water drop first “touches” the surface (Fig. 2 step b), the attractive force produced by the wetting interaction between the water droplet and the surface is recorded as the snap-in force, the stronger the water-surface attraction the stronger the snap-in force. The snap-in force is shown to correlate well to the advancing contact angle $\theta_A$ (Fig. 3a). The correlation is very general including all the surfaces described above.

After the water droplet and the surface made contact, the stage is retracted slowly, a pull-off force is recorded when the water droplet and the surface separates (Fig. 2 step c). Figure 3b plots the pull-off force versus $\theta_R$ for the same set of surfaces. The pull-off force is shown to decrease monotonously as $\theta_R$ increases. The work-of-adhesion of between a liquid droplet and a solid surface is given by $\gamma_{LS}(1 + \cos \theta_R)$ [7] and a good correlation is obtained when the pull-off force is plotted against $\gamma_{LS}(1 + \cos \theta_R)$ [5]. The overall result thus indicates that the water–surface adhesion decreases as $\theta_R$ increases.

Definitions for hydrophilicity, hydrophobicity and superhydrophobicity

Upon closer examination of the plot in Fig. 3b, one may notice that there is a divide of the data at $\theta_R \sim 90^\circ$. The data in the left-hand-side, surfaces 1–7, 9, 12 and 20 are represented by solid diamonds and the data in the right-hand-side, surfaces 8, 10–11 and 13–19 are represented by empty squares. As reported earlier, Samuel et al. [5] actually observed a small residual water droplet after the surface and the water droplet separate for surfaces with $\theta_R < 90^\circ$. The surface is clean after the water droplet retracts for surfaces with $\theta_R > 90^\circ$. Photographs and the schematic showing these two cases are given in Fig. 4. The observation of the tiny residual water droplet after the water–surface separates is indicative of definite affinity. Based on the observed water–surface affinity, a surface can be defined as hydrophilic when $\theta_R$ is $< 90^\circ$ and hydrophobic when $\theta_R$ is $> 90^\circ$.

The remaining question to be answered is why does the surface change from hydrophilic to hydrophobic at the cut-off $\theta_R \sim 90^\circ$. It is important to note that the plot in Fig. 3a indicates that there is always attractive interaction between water and the hydrophobic surfaces even though the attraction is weakening. The fact that no residual water droplet was observed when $\theta_R > 90^\circ$ is attributable to the high cohesion of the water droplet. In the other words, the water droplet prefers to be in the droplet state than wetting the surface due to the small wetting energy. The importance of liquid cohesion in wetting was in fact discussed lengthly in Young’s original essay [1].
Another term that has been tentatively defined in the literature is superhydrophobicity. As noted by Roach, Shircliff and Newton [8], the definition of superhydrophobicity for surfaces having water $\theta > 150^\circ$ is somewhat arbitrary. On the other hand, the result in Fig. 3a actually shows that there is practically no wetting interaction between water and surfaces with $\theta_A \geq 145^\circ$. Hence a surface can be defined as superhydrophobic when its $\theta_R$ is $> 90^\circ$ and $\theta_A \geq 145^\circ$. A 2D representation of the surface definition is given in Fig. 5.

Surface wettability is known to increase as the surface tension of the wetting liquid decreases [9]. As a result, considerable amount of attention has been paid recently to surfaces which are non-wettable against hydrocarbon oil such as hexadecane [10–14]. It is generally believed that a surface that is super repellent against heptane-to-hexadecane should repel most liquids due to their low surface tensions. In the literature, the traditional cutoff points for water has been extended to hexadecane, namely a surface is oleophilic if its hexadecane $\theta$ is $< 90^\circ$, oleophobic if $\theta$ is $> 90^\circ$ and superoleophobicity if $\theta$ is $\geq 150^\circ$. To our knowledge, there is no technical data to support this definition. This has motivated the examination of early data on the wetting and adhesion interactions between hexadecane and several surfaces used in the previous study. The preliminary results are summarized in Fig. 6. Results in Fig. 6a shows that the snap-in (wetting) force decreases linearly as the hexadecane $\theta_A$ increases. An intercept at $163^\circ$ is observed, indicating that surfaces...
with $\theta_R \geq 163^\circ$ will have no affinity with hexadecane. This trend is similar to that observed with water (Fig. 3a). The plot between pull-off force and $\theta_R$ is more scattered and is attributable to the high adhesion between the hexadecane droplet and the probing surfaces. A significant quantity of hexadecane was found transferring to the surface after pull-off. Since the amount of hexadecane that is transferred is expected to increase as the surface adhesion increases, the trend can then be captured as the weight loss during the pull off experiment. Figure 6b shows the relationship between the weight loss of the hexadecane droplet after pull off and $\theta_R$. A much better plot is obtained. The intercept is at $124^\circ$, suggesting that surfaces with $\theta_R > 124^\circ$ should have little affinity with hexadecane. Accordingly, the cut-off between oleophilicity/phobicity for hexadecane is at $\theta_R = 124^\circ$ and a surface is defined as superoleophobic when $\theta_R$ is $>124^\circ$ and $\theta_A$ is $\geq 163^\circ$. The 2D surface definition plot for hexadecane is given in Fig. 7.

Summary and remarks

Upon closer examination of recent wetting and adhesion data between water and a variety of solid surfaces, an improved definition for hydrophilicity and hydrophobicity is proposed. A surface is hydrophilic when its
Fig. 6: Plots of (a) snap-in force versus advancing contact angle and (b) weight loss of the hexadecane droplet after pull-off versus receding contact angle with different surfaces.

Fig. 7: A 2D graphic representation for the definitions of surface oleophilicity, oleophobicity and superoleophobicity.

water $\theta_w$ is $<90^\circ$ and hydrophobic when $\theta_w$ is $>90^\circ$. The driving force for switching from hydrophilic to hydrophobic is the high water surface tension. Additionally, surfaces with $\theta_A \geq 145^\circ$ and $\theta_R > 90^\circ$ can be defined superhydrophobic, as there is practically no affinity between these surfaces and water.

An extension of this methodology to define oleophilicity, oleophobicity and superoleophobicity is put forward based on preliminary data. The cut-off point for hexadecane oleophilicity/phobicity is at $\theta_h 124^\circ$. The surface can be defined as superoleophobic when its hexadecane $\theta_A$ is $\geq 163^\circ$ and $\theta_R > 124^\circ$. Since phobicity originates from the surface tension of the liquid, the larger cut-off $\theta_h$ for hexadecane is consistent with the proposed mechanism as the surface tension of hexadecane is $\approx 2.5$ times smaller than that of water (27.5 mN/m vs. 72.3 mN/m).
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References