WETTING AND EVAPORATION STUDIES ON MOLECULARLY MODIFIED SURFACES

by

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ABSTRACT

Wetting and evaporation of liquid microdroplets on solid surfaces are ubiquitous in nature. Two of the many important factors that influence how a droplet wets and “escapes”, are the chemical composition and roughness of the solid surface. In order to gain a better understanding of these processes as a whole, a systematic study on the factors that influence wetting/evaporation behaviour, including the liquid’s composition, the liquid-solid interface, and the substrate morphology has been carried out in this thesis. In particular, the evaporation profile and its correlation with the wetting hysteresis have been studied using both water and binary mixtures on self-assembled monolayer (SAM) surfaces. Based on surface modification with mixed SAMs in conjunction with microcontact printing and electrochemical deposition techniques, this work aims at a comprehensive and controlled study of how molecular/structural modification dictate the wetting and evaporation behaviour of microdroplets on the surface.

Keywords: wetting hysteresis; evaporation; self-assembled monolayer; electrodeposition; superhydrophobicity
DEDICATION

In loving memory of my dearest grandmother Gladys Hart, a woman of remarkable strength and character. I am thankful for the love, support, and guidance that she gave me throughout the years.
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GLOSSARY

AFM: Atomic Force Microscopy

PDMS: Poly(dimethylsiloxane)

$rms$: Root-mean-square

SAMs: Self-Assembled Monolayers

$\mu$CP: Microcontact Printing

CV: Cyclic Voltammetry
CHAPTER 1: A GENERAL INTRODUCTION TO WETTING STUDIES AND SURFACE MODIFICATION TECHNIQUES

This chapter is a general introduction to the study of wetting/evaporation properties and how such surface properties can be modified and understood. It begins with an overview of the history of the wetting phenomena. Extreme situations of wetting, as in the case of superhydrophobic surfaces are discussed, and literatures pertaining to research work that have “mimicked” this behaviour are noted. Also, the main theories developed to explain wetting behaviour are introduced. Since evaporation studies are a main component of the wetting phenomena, its related literature is summarized next. This thesis also deals with the modification of surface properties (specifically, modification of the chemical composition and surface roughness) to tune the wetting properties; therefore, surface modification methods (used in this work) such as the formation of self-assembled monolayers (SAMs), microcontact printing (μCP), and electrochemical deposition are introduced.

1.1 Objectives and Previous Work

There are many factors to be considered that influence how a liquid wets a surface, among which a surface’s chemical composition and surface roughness play a large role. In order to gain a better understanding of this process as a whole, a systematic study of the factors that influence wetting such as: 1) the liquid’s composition 2) the interface and
3) the substrate morphology, are valuable. The flowchart below outlines the three main chapters of this thesis and their relationship to the study of wetting properties.

Figure 1.1: Thesis flow chart outlining the objectives of this thesis in studying wetting properties in relation to the 1) liquid composition 2) the interface 3) the substrate morphology.

The objective of this thesis is to study the influence that these factors have on wetting phenomena such as static contact angles, evaporation profiles, and wetting
hysteresis of microdroplets on solid surfaces. In these studies, we have used SAMs on gold as model surfaces. Various alkanethiol molecules having different terminal functional groups can be used to modify gold substrates to achieve different surface chemical compositions. Furthermore, alkanethiolate monolayers on gold can be patterned by μCP and used as templates to control the deposition of films in creating surfaces with desired micropatterns and roughness. Thus, these model systems have allowed for a range of surface modification routes from tuning the chemical composition via modification with mixed SAMs, to varying the surface roughness through electrochemical deposition of inorganic oxide films.

The present research builds upon previous work in our lab involving the study of wetting properties. Liu et al have carried out contact angle studies of mixed ω-carboxyalkyl/alkyl monolayers on silicon surfaces and evaluated the acid-base properties of these mixed monolayers upon hydrolysis.\(^1\) It was noted that the water contact angles increased with increasing alkyl chain length for mixed monolayers of unsubstituted alkyl chains and those derivatized with ester groups. With longer n-alkenes such as tetradecene, the ester groups are buried in the hydrophobic “pockets” of the longer methyl terminated chains, resulting in larger contact angles (a more hydrophobic surface). They also monitored the hydrolysis of ester-terminated monolayers on silicon by wetting measurements and their acid-base properties by constructing contact angle titration curves. This work later extended to evaporation studies on gold surfaces modified with alkanethiolate SAMs.\(^2\) Using mixed monolayers with –CH\(_3\) and –OH terminated groups, we were able to “tune” the wetting properties of the surface from hydrophilic (contact angle < 90°) to hydrophobic (contact angle > 90°) and studied the evaporation trend for
these surfaces. For all surfaces, irrespective of their chemical heterogeneity, a mode of “pinning” (constant contact area accompanied by decreasing contact angle) and subsequent “shrinking” (constant contact angle accompanied by decreasing contact area) was observed (Figure 1.2). Furthermore, all surfaces were found to decrease from their initial contact angles to the equilibrium contact angle by the same amount of 10°. Such contact angle variation during evaporation matches the wetting hysteresis, i.e. the difference between advancing and receding contact angles. This led to the finding that the evaporation profile is independent of the polarity of the surface. This previous research forms a solid foundation for this thesis, which aims at a further understanding of the effects that the chemical composition of a surface, surface morphology, and liquid composition have on the wetting and evaporation behaviour of microdroplets on solid surfaces.

![Diagram of droplet evaporation modes](image)

**Figure 1.2:** Two modes of droplet evaporation: (a) Constant contact area mode where the contact area remains constant during evaporation, (b) Constant contact angle mode where the contact angle remains constant during evaporation. (Reproduced with permission from *J. Phys. Chem. B* 2005, 109, 17967-17973. Copyright 2005 American Chemical Society).

Initially in this thesis, the influence that a liquid’s composition has on the evaporation profile was studied. Gold substrates modified with SAMs were used to study the evaporation profile of binary water/alcohol droplets. It was found that mixed liquid
systems follow trends that differ from the evaporation of pure liquids, particularly for the cases where the two liquids have different volatilities.

The influence that the solid/liquid interface has on the evaporation profile and wetting hysteresis was then studied. Gold substrates were modified with SAMs having mixed functional groups and mixed chain lengths to study how molecular modification (chemical composition) and surface roughness (at the molecular level) influences evaporation behaviour of water microdroplets. These results were then compared to conventional substrates often used in wetting experiments. The general findings of this study showed an inclusive trend in the evaporation profile that was observed for all surfaces where there was a switching between a constant contact area mode to a constant contact angle mode. Furthermore, it was found that surface roughness rather than chemical heterogeneity plays a dominant role in the wetting behaviour and had a significant influence in the mode switching behaviour.

In studying how the interface affects wetting, it was found that surface morphology, even at a molecular level has a dominant role in wetting properties. Therefore, we extended our studies to investigate the extent that the surface morphology can be used to tune a surface’s wetting properties while keeping the same chemical composition. Specifically, we examined the effect that the macroscopic roughness of a film patterned with microscale roughness has on wetting properties. We were interested in learning about the range of contact angles that could be achieved by solely manipulating the surface roughness, and the extent that the surface morphology affected wetting properties. In this thesis, by using patterned molecular templates (patterned SAMs on gold surfaces prepared by microcontact printing), we were able to
systematically control the selective deposition of zirconia films onto gold substrates to achieve different patterns/roughness.

1.2 History and Brief Overview of Wetting Properties

There is much to learn from nature in terms of the mechanisms at work that lead to examples of water-repellent surfaces (hydrophobic) and surfaces that attract water (hydrophilic). "Wetting" refers to the phenomenon of a liquid contacting a solid surface. It is an occurrence familiar to all on a daily basis, from the beading of water on car windshields to the rise of liquids in capillaries. A great deal of interest in this topic has been generated owing to the advantages of creating functional surfaces with antifogging or self-cleaning properties and inhibiting contamination, erosion, or snow sticking on surfaces. Wettability is used in fundamental material research to characterize a surface, and is one of the most important properties of a solid surface. If a liquid is wetting, it spreads easily across a surface having a contact angle that is zero or close to zero. This property can be useful in applications such as insecticides, where it's necessary for the liquid to completely wet the leaf to protect it. On the other hand, it is often desirable to have a liquid not wet the surface as in the case of antifogging or water-repellent surfaces. This can be achieved with the application of waterproofing agents that cause the surface to be hydrophobic or even superhydrophobic.

In the early part of the 20th century it became well known that an organic monolayer adsorbed on a solid surface had a profound effect on the wetting properties. This finding would later result in numerous studies where various molecular surface modifications were used to tune the wetting properties; however, little was understood about the observed trends. To gain a deeper understanding of the wetting phenomenon,
the attention began to shift towards understanding the evaporation of liquid droplets from solid surfaces as these two processes are intrinsically connected.\textsuperscript{3-11} The evaporation rate of liquids from solid surfaces measured as the change in mass of the liquid per unit time became the primary focus of many investigations.\textsuperscript{3,8-11} Various substrates and atmospheric conditions were tested in an endeavour to determine if any consensus could be reached between the diverse trends observed. However, a lack of systematic control in these investigations made any generalizations unreliable. In the following sections, brief introductions will be provided for superhydrophobicity, wetting theory, and microdroplet evaporation profiles, topics that are directly related to the work described in this thesis.

1.2.1 Superhydrophobicity in Nature and its Applications

Many plants and animals in nature have been engineered to possess wetting properties viable to their survival. They demonstrate extremes of the wetting phenomena, exhibiting extremely high contact angles notable of water-repellent surfaces. Surfaces with contact angles greater than 150\degree are generally considered as superhydrophobic.\textsuperscript{12, 13}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{superhydrophobicity.png}
\caption{Contact angle in the superhydrophobic regime. The droplet sits on the surface maintaining an approximate spherical shape and having a contact angle of 160\degree (measurement taken on an oxygen-plasma treated Teflon film, provided by OceanNano Technologies LLC.).}
\end{figure}
A notable example of this is the Lotus leaf. When a water-droplet falls on the Lotus leaf the droplet forms a contact angle in the superhydrophobic range (~ 160°). This water-repellency can be attributed to the two scales of roughness present on the leaf: on a larger scale there are micrometer bumps, and also hair-like features on the nanometer scale. In addition, a wax layer over the surface of the leaf enhances its hydrophobicity (lowers the surface energy). The blue Morpho sulkowskyi butterfly also demonstrates the “Lotus Effect”. Closer examination shows that the water-repellency of the wings is also due to its’ specific micro- and nanostructure. The potential uses for water repellent surfaces are far reaching and may find application in self cleaning surfaces, car windshields, paints, and fabrics.

There has been mounting interest in the scientific community to fabricate superhydrophobic surfaces. Many studies have been conducted to “mimic” the behaviour of the Lotus leaf and Morpho butterfly due to the appeal of creating water-repellent materials. Erbil and co-workers have dissolved polypropylene in solvents such as p-xylene to prepare superhydrophobic coatings that can be applied onto solid substrates. Chen et al. have created superhydrophobic SnO₂ nanoporous flower-like structures via thermal processes. It is generally recognized in most studies that a two-tier (micro and nano) roughness is essential for achieving such high contact angles.

1.2.2 Classical Theories of Wetting Properties

Contact angle measurements date back to the 19th century when attempts were made to understand wetting behaviour in terms of the newly found differential calculus. Contact angles give information on both solids and liquids such as their cohesive forces, wetting behaviour, adhesive properties, morphology, and chemical nature. It is a very
surface specific technique and is of great industrial interest. Every year there are hundreds of research papers published where contact angles are used to characterize a variety of surfaces such as wood, paper, polymers, or minerals. Furthermore, the surface tension of a liquid can be measured directly and is quite accurate; however, the surface tension of a solid can only be estimated by indirect analysis via contact angle measurements. A liquid droplet on a flat solid surface under static conditions forms a contact angle which is related to its interfacial free energies. This relationship is given by the classical Young's equation:

**Equation 1.1 - Young's Equation:**

\[ \cos \theta = \frac{(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} \]

Where \( \gamma \) is the interfacial tension of the solid-liquid, solid-vapour, and liquid-vapour interfaces.

![Figure 1.4: The contact angle formed on a surface is described by the classical Young's equation relating the angle to the interfacial tensions of the solid-vapour, liquid-vapour and solid-liquid interface.](image)

Young's equations is formulated by considering a liquid spreading on a solid surface. A liquid in contact with a solid surface spreads to increase the solid-liquid and
liquid-vapour interfacial areas and decrease the solid-vapour interfacial area.\textsuperscript{24} The spreading coefficient, $S$, is defined as:

\textbf{Equation 1.2 - Spreading coefficient}

$$S = -\frac{\Delta G_s}{A} = \gamma_{sv} - (\gamma_{sl} + \gamma_{hv})$$

Where $\Delta G_s$ is the increase in free energy due to spreading. For a liquid that spontaneously spreads across a surface $S$ is positive or zero. When $S$ is negative the liquid maintains a drop shape and has a contact angle $\theta$. This equilibrium contact angle describes the total surface free energy of the system (i.e., $\gamma_{sv}A_{sv} + \gamma_{sl}A_{sl} + \gamma_{hv}A_{hv}$, where $A$ is the interfacial area) at a minimum. For a liquid spreading an infinitesimal amount further over an extra area $dA$, the liquid-vapour interfacial area will be $dA \cos \theta$, and the increase in the free energy of the system is:

\textbf{Equation 1.3 - Increase in free energy due to spreading}

$$dG = \gamma_{sl}dA + \gamma_{hv}dA \cos \theta - \gamma_{sv}dA$$

When the system is at equilibrium, $dG = 0$, the above equation reduces to:

\textbf{Equation 1.4 - The derived Young's equation}

$$\gamma_{sl} + \gamma_{hv} \cos \theta - \gamma_{sv} = 0$$

The above expression can then be rearranged and expressed as Equation 1.1, Young’s equation.

The system minimizes the total surface energy which leads to the formation of the spherical cap geometry and resultant contact angle when the droplet is within a small volume limit (where surface tension dominates over gravity).\textsuperscript{9,25} Under dynamic
conditions where there is movement of the liquid such as in the case of evaporation, there is a slight departure from this relationship.\textsuperscript{5}

Theoretically, the contact angle of a pure liquid placed on an ideal solid surface should have a single value as predicted from Young’s equation; however, practically on composite surfaces there exists an entire range of angles.\textsuperscript{8} The maximum and minimum of these angles is known as the advancing (\(\theta_A\)) and receding (\(\theta_R\)) contact angles and measures the tendency of liquid droplets to advance and recede, respectively, across a surface which is related to the movement of a three-phase (solid-liquid-vapour) contact line.\textsuperscript{6} Therefore, even a flat surface itself does not possess a unique static contact angle; rather the angle observed is dependant on whether the droplet was formed by an advancing front (by increasing the drop volume in steps) or by a receding front (by decreasing the drop volume in steps).\textsuperscript{26} The difference between the advancing and receding contact angles is known as the wetting hysteresis:

\textbf{Equation 1.5 - Wetting hysteresis:}

\[\theta_A - \theta_R = \Delta \theta\]

This hysteresis is a result of the adhesive force between the liquid and solid that was created when the droplet spread on the surface and is due to surface heterogeneities that act to pin the contact line.\textsuperscript{27} When the contact line recedes with a \(\theta_R > 0\), then the liquid detaches from the solid; thus, hysteresis becomes a good gauge of the adhesive properties between liquids and solids. The advancing and receding contact angles are generally determined by the method of Dettre and Johnson.\textsuperscript{28} In this experiment, decreasing the droplet volume until the point where the contact area decreases gives the
receding contact angle ($\theta_R$), and increasing the droplet volume until the point where the contact area increases gives the advancing contact angle ($\theta_A$) (Figure 1.5).

Figure 1.5: Direct measurement of wetting hysteresis. In this method, decreasing the droplet volume until the point where the contact area decreases gives the receding contact angle ($\theta_R$) as shown in the above figure. Alternatively, increasing the droplet volume until the point where the contact area increases gives the advancing contact angle ($\theta_A$).

Furthermore, the correlation that we found previously between evaporation trends and wetting hysteresis can be better understood by considering the volume changes occurring in each process.² We believe that the direct measurements of wetting hysteresis mimics the evaporation process and therefore they are correlated. In our evaporation...
experiments, a droplet formed on a surface has an initial advancing front and, as evaporation proceeds, its volume decreases in constant contact area mode until the receding angle is attained.

An understanding of wetting hysteresis is fundamental to controlling many wetting processes (for example coating, spraying, printing etc). In creating water-repellent surfaces this contact angle hysteresis plays a significant role, more so than that of the static contact angle. Since it becomes desirable to have the droplet move across a surface with very little applied force, this dynamic wettability which is a function of contact angle hysteresis must be taken into account. Although this phenomenon has been analyzed from a thermodynamic perspective, considering the energy barriers between the metastable contact angles, wetting hysteresis is still not well understood. The main reasons for these varied contact angles has been attributed to the chemical heterogeneity, roughness of the surface, and evaporation. On an ideally flat, homogenous surface the contact angle theoretically should be determined based only on the ratio of the contributing interfacial tensions. However, real solids possess both surface roughness and chemical heterogeneities, which give rise to deviations from Young’s equation. As a result other theories were developed to account for both these contributing factors.

The apparent contact angle on a roughened surface was described by Wenzel’s theory. In this model the liquid is assumed to fill the grooves of the roughened surface such that the liquid is in complete contact with the surface. The hydrophobicity on such surfaces increases with increasing roughness by a factor $r$, where $r$ is the ratio of the
actual area of the liquid-solid contact to the geometrically projected area and is thus always greater than unity.\textsuperscript{12,26} Thus Wenzel’s equation follows for a “wetted” surface:\textsuperscript{26}

**Equation 1.6 - Wenzel’s equation:**

\[ \cos \theta' = r \cos \theta \]

For a roughened surface composed of rectangular pillars the roughness is calculated as follows:

**Equation 1.7 - Roughness factor:**

\[ r = \frac{(a + b)^2 + 4ac}{(a + b)^2} \]

Where \( a \) is the pillar width, \( b \) is the width between pillars, and \( c \) is the pillar height (Figure 1.6). In this case the interaction of the liquid with the surface topography leads to a highly “pinned” droplet and large values of contact angle hysteresis such that substantial force is needed to initiate droplet movement.

![Figure 1.6: Pillar-like structure for the determination of roughness factors. Where \( c \) is the pillar height, \( a \) is the pillar width, and \( b \) is the width between pillars.](image)

When a droplet sits on a rough surface such that the liquid is completely lifted up by the roughened features and does not fill the grooves, another theory must be used to describe the contact angle.\textsuperscript{5} Cassie and Baxter’s Theory describes the contact angle of a droplet sitting on a heterogeneous surface.\textsuperscript{12}
Equation 1.8 - Cassie’s Equation:

\[
\cos \theta' = f_1 \cos \theta_1 + f_2 \cos \theta_2
\]

\[
\cos \theta' = f \cos \theta + (1 - f) \cos 180° = f \cos \theta + f - 1
\]

Where \( f_1 \) and \( f_2 \) are the fractional areas of the two different surfaces. For a rough surface where the droplet sits on fractional areas consisting of the solid surface and air, the equation is modified when \( f_2 \) is the fractional area of trapped air. In this equation \( f \) becomes the fractional area of the solid-liquid interface and the air-liquid interface is given by \((1 - f)\). Since droplets are suspended on top of the surface features and voids of air, the contact angle hysteresis can be greatly reduced, characteristic of super-repellent surfaces with very large apparent contact angles (140 to 180°).^27

Figure 1.7: (A) Wenzel’s Case: the droplet wets the surface intruding the pillars (B) Cassie’s Case: the droplet sits on top of a composite surface (C) Cassie’s Case: The droplet sits on top of a composite surface composed of air and the substrate.

Contact angles on rough surfaces can be described by either Wenzel’s or Cassie’s theory and depending on whether the system is “wetting” or “non-wetting” the model that fits best is adopted.^26,32 However, in the literature it is not certain which theory correctly accounts for the apparent contact angles on rough surfaces since on the same rough surface both cases are possible, corresponding to these two different models.\(^5\) The two distinct contact angles on the same surface can both be stable equilibrium positions.
giving local energy states; however, whether a wetted surface or a composite surface
gives a global minimum energy is dependant on the geometric parameters of the
surface.\textsuperscript{26}

Furthermore, there is some discrepancy in the literature concerning the near
spherical droplets that form on super hydrophobic surfaces as to which regimes obey
Wenzel’s or Cassie’s mode as they both describe the enhancement of contact angles.
This is due to the very different adhesion behaviours between a drop that follows
Wenzel’s mode and one that follows Cassie’s mode.\textsuperscript{33} A droplet in Wenzel’s mode is
extremely pinned where enhancement of the hydrophobicity can be thought of in two
ways: In Wenzel’s model, a rough material has a higher surface area than a smooth one
and in Cassie’s mode trapped air increases the hydrophobicity.\textsuperscript{15} A drop with a contact
angle of 170° and in agreement with Cassie’s theory, when physically pressed the contact
angle decreases to 130° and is in agreement with Wenzel’s theory.\textsuperscript{34} Therefore, it is
possible to have a transition between the two regimes.\textsuperscript{33}

1.3 Evaporation of Microdroplets from Solid Substrates:

Evaporation of water microdroplets is a fundamental phenomenon in nature that is
necessary to many life processes. Studies of evaporation processes are useful in
understanding complex systems such as clouds, fogs, engines etc.\textsuperscript{11} The first recorded
study of the evaporation process of water on a surface covered with an insoluble
monolayer was conducted by Hedestrand in the early 1920’s.\textsuperscript{35} Since then, studies have
focused primarily on the evaporation rate of liquids from solid surfaces, which is
traditionally measured as the change in mass of the liquid per unit time.\textsuperscript{3,10,11} This
allowed the observation of how the state of the fluid changes as evaporation proceeds.\textsuperscript{3}
The assumption made is that the vapour concentration at the liquid vapour interface is equal to the equilibrium concentration (the saturation vapour at the temperature of the drop). Whereas the local atmosphere is generally under-saturated in the vapor. Therefore, the rate of evaporation of a stationary spherical drop is determined by the rate of diffusion of the vapour from the interface of the droplet to an infinite distance from the interface. Moreover, molecules along the contact line have additional energy because their environment is different compared to the bulk. It is observed that the rate of evaporation is proportional to the radius of the droplet rather than the surface area and that for a larger radius of the liquid solid interface, the faster the evaporation rate. Furthermore, this droplet evaporation is accompanied by a decrease in contact angle.

Picknett and Bexon in 1977 extended the investigation beyond evaporation rates, which led to the classification of the overall process into two distinct modes (i.e., the variation of the droplet shape as a function of time). The first is the constant contact area mode, for which the contact area remains unchanged during evaporation while the contact angle decreases ("pinning") (Figure 1.2). The second is known as the constant contact angle mode where the contact angle remains unchanged during evaporation but the contact area decreases ("shrinking"). They proposed that during evaporation the first mode dominates until the contact angle decreases to a constant value, and at this point the evaporation switches to the second mode; however, this was not shown experimentally.

Later, Birdi and Vu studied the evaporation of water droplets on two "smooth" surfaces: glass and Teflon. Their results led to two generalizations: (i) if the contact angle $\theta < 90^\circ$, the constant contact area mode is observed, and (ii) if $\theta > 90^\circ$, the
constant contact angle mode would be expected.\textsuperscript{3} It should be noted that the variation of
the morphology and chemical composition of these surfaces were not considered.

Two years later, Shanahan and co-workers studied the evaporation of water on
polymeric substrates (i.e., poly(tetrafluoroethylene), polyethylene, glass, and epoxy resin)
with a range of roughness under different atmospheric conditions.\textsuperscript{36} They monitored the
height, diameter, and contact angle of water droplets during evaporation in both open and
closed systems and observed complex evaporation profiles for these systems. The process
can be divided into four stages, with each stage showing different changes in the water
droplet shape. For example, when the atmosphere is not saturated, there is a pronounced
decrease in height and contact angle while the drop diameter remains constant. This is,
especially, the first mode (constant contact area) observed by Picknett and Bexon.\textsuperscript{10}

1.4 Chemical Heterogeneity vs. Surface Roughness in Creating
Tuneable Surfaces:

1.4.1 Chemical Modification of Surfaces using Self-Assembled Monolayers

Controlled chemical modification of solid surfaces allows for the systematic study
of the influence of surface modification on wetting properties. SAMs continue to be a
prevailing simple, room-temperature method to chemically modify solid substrates.\textsuperscript{37,38}
Their synthesis, structure, and properties have been extensively studied since the
1980’s.\textsuperscript{39} In particular, SAMs of alkanethiols on gold are well studied and have been used
as model systems to study interfacial properties such as wetting, adhesion, and protein
adsorption.\textsuperscript{40} Organic thiols from solution readily adsorb onto gold and self-assemble to
form ordered monolayers over relatively large areas,\textsuperscript{41} with the driving force of this
reaction being the strong interaction between gold and sulfur.\textsuperscript{42} Individual subunits arrive
at the final structure by equilibrating to the lowest energy form. Because the final self-assembled structures are close to or at the thermodynamic equilibrium they not only form spontaneously, but also reject defects.\textsuperscript{40} It is believed that this Au-S bonding is sufficiently stable and strong, having bond energies of approximately 48 kcal mol\textsuperscript{-1}. The proposed chemistry occurring between the gold and thiol molecules is:\textsuperscript{42}

\textbf{Equation 1.9 - Formation of alkanethiolate SAMs on gold:}

\[ R - SH + Au_n^0 \rightarrow RS^- - Au^+ + \frac{1}{2} H_2 + Au_{n-1}^0 \]

Though it is believed that a thiolate (Au-SR) is the eventual species that is formed on the gold surface by adsorption of thiols, the reaction mechanism remains unclear and debatable.\textsuperscript{31} For thiols of the form CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{n-1}SH with n = 4-17, the alkyl chains extend from the plane of the surface in an all-trans configuration and are tilted approximately 30° away from the normal of the gold surface to maximize the van der Waals interaction between nearby methylene groups.\textsuperscript{31,40}

Self-assembly is now a proven and versatile strategy to modify the chemical properties of metallic interfaces.\textsuperscript{4,43} Of greater use is that the chemical property of a surface can be tuned by varying the composition of a mixed monolayer;\textsuperscript{4} for example, they can be composed of both hydrophobic (-CH\textsubscript{3}) and hydrophilic (-OH) terminal groups.
In wetting and evaporation studies the surface modification with SAMs exhibits three notable advantages: 

1) the monolayer films fully cover the surfaces with highly oriented and closely packed molecules; 
2) the SAMs allow for controlled chemical heterogeneity on the surface; 
3) the wetting properties (i.e., the surface energy) can be tuned as a function of the relative concentrations of the components (Figure 1.8).

The modification with SAMs also provides a relatively stable surface. It has been shown that in most cases, immersion of the substrate in the deposition solution for overnight, a number of weeks, or even months resulted in the same contact angle being measured on thus formed monolayer surfaces. Extensive studies have been done on the structural characterization of SAMs by various surface analysis techniques such as infrared (IR), x-ray photoelectron spectroscopy (XPS), and ellipsometry. Studies of mixed monolayers with –OH and –CH₃ terminal groups have shown that generally the ratio of the two components in the mixed monolayer is not the same as in solution, but rather is dependant on the relative solubilities of the components in solution in addition to the interaction between the tail groups in the monolayers. Furthermore, these two components do not phase segregate into macroscopic islands or single component
domains that are large enough to influence the contact angles (islands would have to be greater than 0.1 μm in size to cause observable hysteresis). 31

It should be noted that SAMs on gold allow for the possibility of studies of not only interfacial and wetting properties, but also protein adsorption, electron transfer, molecular recognition, and multilayer formation. 4 The ability of SAMs to protect metal substrates against chemical agents has also been exploited. 45 SAMs can be selectively patterned using microcontact printing (μCP) techniques, which serve as molecular templates for selective chemical etching or selective deposition. 40

1.4.2 Micro/Nano Fabrication in Creating Surfaces with Tuneable Wetting Properties

The wettability of a surface is a function of its roughness and chemical composition; therefore, microfabrication techniques have been employed previously to explore this dependence. 46,47 As outlined in the review of Xia and Whitesides on soft-lithographic techniques, μCP is a straightforward, low cost method to form patterns of SAMs on surfaces using elastomeric poly(dimethylsiloxane) (PDMS) stamps. 40 In this method the prepolymer of the elastomer is poured over a master typically patterned with micrometer sized dimensions (usually fabricated by photolithography techniques). 48 The elastomer is then cured and peeled off. The PDMS stamp is then inked with a solution of 1-5 mM of alkanethiol and then brought into contact with the surface briefly. This results in the transfer of the alkanethiol from the stamp onto the gold, forming patterned SAMs on the surface. The attractiveness of μCP is it's ability to rapidly produce micro-features with a potential resolution of < 100nm, and it's usefulness in large area patterning. 40
These patterned SAMs can serve as resists from attack by wet etchants to pattern surfaces. They have been exploited to direct the nucleation and growth of metals by selective chemical vapour deposition (CVD) or by electroless plating. It has been shown that nucleation of the depositing materials only occurs in either regions not covered by the SAMs or at defect sites.

1.4.3 Electrochemical Deposition for Creating Patterned Surfaces

Nanofabrication has generated a great deal of interest in recent years with studies focused on various methods to fabricate micro and nano-structures on diverse substrates. One such method which has been gaining attention in recent years as a useful method for the formation of nanostructured materials is electrodeposition. As a simple method, it has been demonstrated to be attractive in the formation of oxide films such as ZrO₂, TiO₂, and ZnO to name a few. Preparation of metal oxide films by electrodeposition from aqueous solution has many advantages: 1) thickness and morphology can be controlled by the electrochemical parameters; 2) fairly uniform films can be made on substrates of complicated shapes; and 3) low cost equipment. It allows for the control of the patterning and uniform deposition of metal oxide films, which is key to the development of technologically useful devices.

One mechanism for the deposition of metal oxide coatings is cathodic electrodeposition. This cathodic process generates base at the electrode surface, typically through the following reactions:
Equation 1.10 - Electrochemically generated base:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad -0.83 \text{ V vs. SHE} \]
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad +1.23 \text{ V vs. SHE} \]

The base generated at the cathode surface can then hydrolyze metal ions leading to the formation of the metal hydroxide at the electrode surface. This technique has been used to prepare zirconia thin films, which finds applications in corrosion resistant coatings, thermal barrier coatings on metallic alloys, and catalysts. Doped zirconia has also been used in solid-oxide fuel cells and oxygen sensors.

In the past, SAMs have been used as model surfaces for oxide thin film deposition. It has been shown that SAMs provide suitable functionality to initiate growth of these films. Aizenberg et al. have shown that SAMs having different terminal functional groups such as -OH, -COOH, -SO$_3$H induces the nucleation of calcite in a controlled orientation. In studies of the electrochemical deposition of zirconia on gold surfaces it was demonstrated that the SAMs have a significant effect on the orientation and size of the film compared to bare gold surfaces. Aslam et al. found that a dithiol monolayer covered on a gold surface resulted in a highly oriented monoclinic ZrO$_2$ film which may be induced by the hexagonal structure of the monolayer; however, when the monolayer was thermally decomposed after annealing, this orientational preference is lost. Yu et al. have found that gold surfaces modified with SAMs of varying functionalities could be used along with specific electrochemical parameters to control the film formation of zirconia. Studies have shown that these films are often found in the hydrated form as zirconia hydroxide. In the literature, thermogravimetric analysis (which shows substantial water loss) and FT-IR analysis along with deuterium exchange studies have shown that these films are hydroxyl terminated.
In the past few years, metal oxide films prepared electrochemically have been used to create surfaces with tuneable wetting properties. This has led to the creation of superhydrophobic and superhydrophilic surfaces. Zhu and co-workers prepared conductive hydrophobic ZnO thin films having contact angles of \(-128^\circ\) which increased to \(-152^\circ\) upon organic modification.\(^{39}\) In comparison, “flat” films had a contact angle of only 109°. Of great interest, is that metal oxide films are being used to create smart surfaces having a wettability that can be switched from superhydrophobic to superhydrophilic.\(^{60}\) This has been demonstrated by Jiang et al. who electrochemically deposited tungsten oxide films onto indium tin oxide (ITO) glass.\(^{61}\) The morphology of the films were controlled by varying the pH of the precursor solution. The resultant superhydrophobic films were made superhydrophilic after exposure to UV irradiation. Furthermore, aligned nanorod films of SnO\(_2\) were made, having contact angles of 154°, which changed to 0° upon exposure to UV irradiation.\(^{62}\) By keeping these films in the dark for a certain time, the superhydrophobic state could be recovered.

1.5 References


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CHAPTER 2: EVAPORATION OF MICRODROPLETS OF ETHANOL-WATER MIXTURES ON GOLD SURFACES MODIFIED WITH SELF-ASSEMBLED MONOLAYERS*

The wetting property and evaporation behaviour of ethanol-water mixtures of various concentrations on gold surfaces modified with 1-decanethiolate self-assembled monolayers (SAMs) were studied by digital contact angle analysis. It has been shown that the initial contact angle decreases monotonically with increased concentration of ethanol in the mixture. Evaporation studies revealed a general trend with an initial increase in contact angle accompanied with a decrease in contact area, then a constant contact angle accompanied with a slower, linear decrease in contact area. At the very beginning of the evaporation process, the contact angles showed a rapid decrease for the microdroplets of a binary mixture with equal volume fractions (i.e., 50% ethanol). Three distinct stages of the evaporation profile for the ethanol-water mixtures were observed, which differ from the inclusive "pinning" and "shrinking" behaviour observed for the pure liquid case. Ultimately, the study makes possible the use of an evaporation profile to monitor the change in concentration of a binary system and allows a better understanding of the interactions between liquid microdroplets with solid substrates.

2.1 Introduction

The goal of surface chemists studying the evaporation of sessile drops on a substrate surface was to clearly define and measure certain parameters required to completely model the evaporation process beyond mass/volume changes. Picknett and Bexon monitored the changes in mass and constructed an experimental profile of a microdroplet of methylacetoacetate evaporating on a poly(tetrafluoro)ethylene (Teflon) surface.\textsuperscript{1} They observed two evaporation modes: constant contact angle with decreasing contact area, and constant contact area with decreasing contact angle. Birdi and Vu explored the correlation between surface wetting properties and their effects on the evaporation behaviour of water microdroplets.\textsuperscript{2,3} Thereafter, several research groups have intensively studied the evaporation behaviour of sessile microdroplets both experimentally and theoretically,\textsuperscript{4-13} the use of varied substrates (with different chemical and morphological properties) reveals a lack of consistency in their observations and interpretations.

Our attempt in resolving these fundamental drawbacks in previous experiments is to use gold surfaces modified with SAMs as model substrates.\textsuperscript{14,15} We have found that, regardless of the composition of the monolayers (i.e., the hydrophobicity of the surface), the evaporation profile of water microdroplets follows an inclusive trend from "pinning" (constant contact area with decrease in contact angle) to "shrinking" (constant contact angle with decrease in contact area).\textsuperscript{15} We have experimentally confirmed that the "sudden" switch between the two modes is governed by the wetting hysteresis. In the next chapter, we extend these investigations to mixed monolayers of different chain
lengths and for comparison also studied conventional solid materials (silicon wafer, plastics, and glass slides).\textsuperscript{14}

Herein, we use these model substrates (i.e., gold surfaces modified with SAMs) to explore the evaporation behaviour of microdroplets of binary mixtures, a topic that has not yet been thoroughly investigated.\textsuperscript{16,17} Rowan et al. pioneered the evaporation studies of 1-propanol/water mixtures on poly(methyl methacrylate) in 2000.\textsuperscript{16} Particularly, mixtures were made below, at, and above azeotropic composition, which allowed for a range of concentrations encompassing solutions with both excess water and excess 1-propanol. Two different evaporation trends were observed depending on whether the composition was below or above the azeotropic composition in addition to a transition mode observed at azeotropic composition. Recently, Sefiane et al. studied the evaporation behaviour of ethanol-water mixtures on a rough Teflon surface and proposed a three-stage "model" to describe the entire process.\textsuperscript{17} However, there are fundamental limitations with their work; first, the use of a rough and uncontrolled Teflon surface as a substrate to understand the evaporation is highly undesirable, as it has been shown recently that the evaporation profile is significantly influenced by the morphology of the surface.\textsuperscript{14} In addition, difficulties in attributing all the evaporation stages to any known physical phenomena prevents a clear rationale in explaining the significance of the proposed model for binary systems. It has been shown in our previous work that SAM-modified surfaces are suitable model surfaces for the study of the evaporation of binary solutions, which lay the fundamentals of exploring more sophisticated systems that are of practical importance. For example, the evaporation "pattern" of multiplex solutions of
biomolecules is critical to the formation of uniform probe spots in the fabrication of DNA microarrays via either ink-jet printing or robotic spotting protocols.\textsuperscript{18,19}

\section*{2.2 Experimental Section}

Gold substrates (regular glass slides first coated with 10 nm Cr, followed by 100 nm Au) were purchased from Evaporated Metal Films (EMF) Inc. (Ithaca, NY), and 1-decanethiol (96\%) was from Aldrich. Deionized water (\(> 18.3 \text{ M} \cdot \Omega\)) was produced from a Barnstead EasyPure UV/UF compact water system (Dubuque, IA). The gold slides were cleaned by immersion in piranha solution (3:1 mixture of concentrated H\textsubscript{2}SO\textsubscript{4} and 30\% H\textsubscript{2}O\textsubscript{2}) for 5 min at 90\°C, followed by rinsing with copious amounts of deionized water. The cleaned gold plates were incubated in a deposition solution of 1 mM 1-decanethiol solution in 95\% ethanol for 24-48 h and subsequently washed with 95\% ethanol and dried with N\textsubscript{2}. Ethanol-water mixtures with volume-to-volume concentrations of 25, 50, and 75\% were prepared from deionized water and absolute ethanol (Commercial Alcohols Inc., ON) for the evaporation studies.

A digital AST Optima contact angle system with a horizontal light beam to illuminate the sample was used to measure contact angles and to monitor the evaporation process. Microdroplets with volumes of 2.0 ± 0.3 \(\mu\text{L}\) from various ethanol concentrations were delivered to the modified gold substrates using micropipettes and were allowed to completely evaporate under ambient conditions (22.7 ± 1.5 °C with a relative humidity of 40-50\%). This small deviation in the relative humidity was not found to influence the evaporation trend since the focus of this study monitors the change in droplet shape (which is dominated by the interfacial tensions) rather than the evaporation rates which are more sensitive to the changes in relative humidity. Enlarged optical images were
taken by using the manufacture software in 1 min intervals between each data point; however, 30 or 15 s intervals were also used if a more accurate qualitative graphical depiction of the data was required.

2.3 Results and Discussion

![Graph](image)

Figure 2.1: Plot of initial contact angles of microdroplets of ethanol-water mixtures on gold surfaces modified with 1-decanethiolate SAMs. The bottom pictures illustrate the drop shape changes as the concentration of ethanol varies: concentration % of ethanol (from left to right) are 0, 25, 50, 75, and 100.
The wettability of a liquid microdroplet on a solid surface is described by a measure of its contact angle, which depends on the interfacial surface tensions between the solid, liquid, and vapour phases. However, an accurate and ubiquitous determination of contact angle is not always straightforward, as it is influenced by many factors, especially when evaporation of the liquid drop is involved. In the present study, microdroplets of ethanol-water mixtures were spread and allowed to evaporate on gold substrates that were modified with 1-decanethiolate SAMs under ambient conditions; the changes in the contact angle, contact area, and the drop volume as a function of time were monitored with a digital contact angle apparatus. As shown in Figure 2.1, the initial contact angle of the microdroplet decreased from $109 \pm 2$ to $35 \pm 2^\circ$ as the concentration of ethanol increased from 0 to 100% (vol %).

Due to the hydrophobicity of the surface (-CH$_3$ terminated), such a trend is naturally predicted since it is favourable for ethanol molecules to "wet" the surface. Ethanol has a vapour pressure higher than that of water at room temperature, therefore, the surface of the droplet and surrounding vapour will have a richer content of ethanol molecules. As the concentration of ethanol in the solutions is increased, it is believed that a larger proportion of ethanol will be found at the extremities of the drop and will significantly contribute to the interfacial energies resulting in a decrease of the initial contact angles (Figure 2.1). Furthermore, a near linear relationship (monotonic decrease) is found when the contact angle was plotted against the concentration of ethanol, indicative of a direct correlation between the interfacial properties of the liquid and its composition. This empirical relationship is of practical significance because it may serve
as a standard working curve, allowing us to directly estimate the composition of a binary mixture by measuring its contact angle on a specific surface.

In our previous studies, it was shown that the evaporation of water microdroplets follows an inclusive trend, that is, from “pinning” to “shrinking”. We proposed that this sudden switch in the evaporation mode is governed by the wetting hysteresis, that is, the difference between the advancing and receding contact angles ($\Delta \theta = \theta_A - \theta_R$), which can be directly determined by the method of Dettre and Johnson. It has been confirmed experimentally that the evaporation hysteresis of water, $\Delta \theta_{\text{evap}}$, that is, the difference between the "equilibrated" and the initial contact angle, was an accurate estimation of $\Delta \theta$ from direct measurements. Our previous results also indicated that, regardless of the hydrophobicity of the surface, the evaporation hysteresis is always approximately $10 \pm 2^\circ$ for SAM-modified gold substrates. The present results are consistent with the above finding for microdroplets of pure water; as shown in Figures 2.2 and 2.3, the evaporation process shows an apparent switching between the pinning and shrinking modes, and the difference between initial and equilibrated contact angles is about $10^\circ$. However, when microdroplets of binary mixtures (ethanol-water solutions) were evaporated on 1-decanethiolate SAMs on gold, very different trends were evident. In all cases, we observed a general increase in contact angle during the first several minutes accompanied by a decrease in contact area, followed by a relatively constant contact angle accompanied by a slower, linear decrease in contact area. We believe the origin of such a trend lies not on the evaporation hysteresis of the binary mixture but rather, on the differential rates of evaporation of the two compounds. As seen from the relationship between contact angle and ethanol concentration shown in Figure
2.1, an increase in contact angle during the evaporation process indicates that the mixture has become more water-rich. This is consistent with the fact that the rate of ethanol evaporation is higher than that of water (as predicted from their different boiling points/vapour pressures). The evaporation process of the binary mixture is analogous to a distillation process where the more volatile component is being evaporated initially (entering the vapour phase), leaving behind a droplet that becomes increasingly rich with the less volatile component.\textsuperscript{24} In comparison with pure liquids, our data of the mixtures suggest that the plateaus of the contact angle are indicative that all the ethanol has evaporated, leaving only water remaining in the droplet. As shown in Figure 2.2, regardless of the initial contact angle of any of the concentrations of ethanol, the contact angles for all the tested systems (25, 50, and 75\%) increase to approximately 100°, which is very close to the equilibrated contact angle in the evaporation profile of pure water microdroplets. This further confirms that the ethanol fraction evaporated first, hence increasing the water fraction in the solution leading to an increase in the contact angle. These results are consistent with the observations by Rowan et al. on the evaporation of water/1-propanol mixtures on PMMA substrates.\textsuperscript{16} They have discovered that, below the azeotropic point, the microdroplets of the mixtures initially wet the surface followed by the contact angle increasing to a maximum before decreasing as evaporation proceeds. It should be noted that the ethanol-water mixtures studied here were all below the azeotropic composition (95\% ethanol and 5\% water).\textsuperscript{24}

A close look at the initial contact angle increase phase of the evaporation curves (shown in Figure 2.2) illustrates that the change in contact angle at the very early stage (first few minutes) is distinctive. It shows up either as a slower increase in comparison
with the general increasing trend or a rapid decrease (for the 50% ethanol solution in particular). The other feature in Figure 2.2 is the sharp decrease in contact angle at the final stage, which is solely due to the complete consumption of the droplet and is not likely governed by any of the aforementioned phenomena.

Figure 2.2: Plot of contact angles as a function of time for the evaporation of microdroplets of ethanol-water mixtures on SAM-modified gold surfaces. (The percentages show the amount of ethanol in the mixture).

As shown in Figure 2.3, the initial contact areas of the droplets are shown also to be dependent on the concentration of ethanol. For higher concentrations of ethanol, the spreading of the microdroplet on the SAM surface is naturally more pronounced (resulting in a large contact area).
Figure 2.3: Plot of contact area as a function of evaporation time for the microdroplets of ethanol-water mixtures on gold surfaces modified with 1-decanethiolate SAMs.

In all cases, two stages are observed for the evaporation of ethanol/water binary systems when focusing from the perspective of contact area: (1) a rapid nonlinear decrease and (2) a subsequent slower, linear decrease. Corresponding to the contact angle changes (shown in Figure 2.2 and discussed above), we believe that the origin of the initial rapid nonlinear decrease in contact area is due to the faster evaporation of the ethanol fraction, thereby increasing the surface tension of the solution that leads to a decrease in contact area. The later, slower linear decrease in contact area mirrors the trend observed for water microdroplets, which infers that essentially at this stage the
evaporation of water is being monitored. Despite what was previously concluded regarding the existence of mainly water during the plateau of the contact angle, Figure 2.3 shows that the slope of the final linear decrease in contact areas increases in absolute magnitude as the concentration of ethanol increases. This implies that the smaller the amount of water contained in the initial system, the faster the contact area decreases.

![Figure 2.4: Plot of volume as a function of evaporation time for the microdroplets of ethanol-water mixtures on gold surfaces modified with 1-decanethiolate SAMs.](image)

Droplet volume versus unit time was also plotted for all five solutions (Figure 2.4). In all cases, the drop volume decreased nonlinearly over time. Since changes in droplet volume directly correspond to the rate of evaporation, a few conclusions are evident from
these data: (1) the rate of evaporation increases as the ethanol concentration increases, which is indicated by the different lifetimes of the droplets. For example, a pure water microdroplet takes about 25 min, while for pure ethanol, it is only about 1 min; (2) the rates of evaporation for all non-100% ethanol systems were similar (similar slope) near the end of the evaporation process, which suggests that only one component is present at the terminal stages of evaporation; (3) the rates of evaporation for the three mixtures near the end of the evaporation process are similar to the rate of evaporation of water, which reaffirms that only water remains in the system near the termination of the evaporation process. It is known that the evaporation of pure droplets proceeds isothermally and can be described by steady-state theory where the vapour pressure is determined by the concentration of the component being evaporated from the surface of the droplet to an infinite distance, the surface-to-volume ratio of the droplet, and the diffusion constant of the evaporating constituent in the gas phase.\textsuperscript{26} As shown by Hopkins et al., for ethanol-water mixtures, steady-state theory fails as heat transfer from the surroundings to the droplet is not adequate to maintain a steady droplet surface temperature.\textsuperscript{26,27} They have suggested that the fast evaporation rates of the more volatile component can result in nonisothermal behaviour in which the surface undergoes a decrease in temperature in comparison to the interior as the droplet undergoes evaporative cooling.\textsuperscript{27} This temperature gradient results in convective flow within the droplet during evaporation, leading to a greater flux of ethanol molecules to the surface due to its higher vapour pressure. Therefore, in the initial stages of binary mixtures, the rapid decrease in volume is attributed to the loss of the more volatile ethanol to the vapour phase; as a result, the composition of the solution changes as evaporation proceeds. As the droplet decreases in
concentration of ethanol molecules, water molecules can more readily flow to the droplet surface. In the later stages of evaporation when the droplet consists largely of water, the rate of change of volume decreases due to water having a lower vapour pressure in comparison to that of ethanol. This observed change in evaporation rate with time is indicative of an unsteady-state evaporation process in comparison with steady-state evaporation processes where the evaporation rate is constant with time.

Mode 1: Pinning

Mode 2: Evaporating

Mode 3: Shrinking

Figure 2.5: A three-mode model to describe the evaporation behaviour of ethanol-water mixtures on SAM-modified gold surfaces.

Sefiane et al. proposed a three-stage model to explain the evaporation behaviour of ethanol-water solutions on a poly(tetrafluoro)ethylene (Teflon) surface. We noted that there are similarities between the observations in the present study and those reported by Sefiane et al., in particular, the different modes in the contact angle/area changes
during the entire evaporation process. Nevertheless, they observed a more pronounced
decrease of the contact angles at the very beginning, especially when the concentration of
ethanol in the droplet is not high (e.g., 25%). The data for water evaporation also show
that the droplet remained pinned for a longer period of time in comparison with our data.
We believe this is due to the different roughness factors of the two surfaces (Teflon
versus SAM-modified gold).¹⁴

Herein, we can further elaborate and simplify the three-stage (mode) evaporation
process as depicted in Figure 2.5, which deviates but closely correlates to the two modes
observed for the pure water system reported previously.¹⁵ The first mode is a pinning
process; that is, the contact angle briefly decreases, while the contact area remains
constant. This mode is governed by the wetting hysteresis of the binary mixture and is
particularly evident when the concentration of ethanol is neither too low nor too high.
This is clearly seen in the evaporation of 50% ethanol in which a subtle initial decrease in
contact angle is observed. Stage 2 corresponds to an increase in the contact angle
accompanied by a rapid decrease in contact area, which can be attributed to the faster
evaporation rate of ethanol in the binary system, hence increasing the surface tension of
the system; therefore, the contact angle increases while the contact area decreases. We
expect that only water is responsible for the evaporation stage 3, which resembles the
shrinking behaviour of pure water microdroplets observed previously.¹⁵ In this case, the
contact angle remains relatively constant, but the contact area decreases linearly. Unlike
1-propanol/water mixtures,¹⁶ any studies of compositions above the azeotropic point are
not feasible, as they relate to a very high concentration of ethanol (>95%). In that case,
the evaporation process of microdroplets is rather fast (Figure 2.4, inset), which makes the contact angle measurements difficult.

2.4 Conclusion

In summary, we have shown that the evaporation mode changes of microdroplets of binary solutions are dominated by both wetting hysteresis and the initial evaporation of the more volatile component. By monitoring the evaporation of microdroplets of ethanol-water mixtures at various concentrations, we were able to observe systematic, sequential changes in the contact angle, contact area, and the volume of the microdroplets, which can be described as three distinct evaporation stages. The different modes correspond to the varied evaporation periods, for which wetting hysteresis domination is taken over first by the evaporation of the more volatile component, and subsequently by the evaporation of the other fraction. More importantly, it has been shown that SAM-modified surfaces are suitable model surfaces for the study of the evaporation of binary solutions.

2.5 References

CHAPTER 3: WATER MICRODROPLETS ON MOLECULARLY TAILORED SURFACES: CORRELATION BETWEEN WETTING HYSTERESIS AND EVAPORATION MODE SWITCHING*

In this chapter the evaporation of water microdroplets from solid surfaces was studied using digital contact angle analysis techniques. An inclusive trend for the evaporation process, that is, a switch from the initial constant contact area to the subsequent constant contact angle mode was observed for all surfaces examined; including mixed self-assembled monolayers (SAMs) on gold and "conventional" surfaces such as silicon wafers, polycarbonate, and Teflon. More importantly, it has been shown that the change in contact angle during the evaporation process (i.e., evaporation hysteresis, $\theta_{\text{evap}}$, the difference between the initial and "equilibrated" contact angle) correlates well with the wetting hysteresis determined directly (i.e., measuring the advancing and receding contact angles on these surfaces by changing the drop volume). The comparison between mixed SAM surfaces and conventional solids allowed for the study of how the surface interface influences wetting/evaporation. It was found that the evaporation/wetting hysteresis is dominated by the roughness (from nanometer to micrometer scale) rather than the chemical heterogeneity of the surface. The evaporation rates of water microdroplets on these surfaces were also monitored and modelled.

3.1 Introduction

Thus far, pioneering studies have suggested that an understanding of the water evaporation phenomenon requires knowledge of the wetting properties of the surface, particularly the wetting hysteresis. The wetting hysteresis is a result of the adhesion created between the liquid and solid during spreading/receding.1 Since the work of Young in the early 19th century on the contact angles of liquids on smooth solid surfaces, a significant amount of research has been devoted to understanding this common dynamic process by studying how surface defects and chemical heterogeneity affect both the adhesive nature and contact angle hysteresis of water droplets.2-4 Since the observation that there exists a range of contact angles on surfaces rather than the single value predicted by Young's theory, numerous experiments have been done to understand this apparent deviation which is still not well understood.5

The advancement of self-assembly techniques has provided an opportunity to study the effects of chemical heterogeneity and molecular level roughness on wetting properties.6,7 Recently, Extrand studied the wetting properties of polyamide and polyethylene surfaces and suggested that roughness does not strongly influence wetting hysteresis, but rather it is dominated by the molecular interactions between the liquid and the solid surface.1 However, our group8 and others9-11 have demonstrated that in mixed SAMs containing polar and nonpolar components of similar chain length, the wetting hysteresis is not correlated to the polarity or chemical composition of the surface. Although the experimental conditions differed in regard to the relative humidity and incubation time, the general findings suggested that chemical heterogeneity does not dominate contact angle hysteresis.8-11 Contrasting results were obtained by Semal et al.
who found that the wetting hysteresis was maximal on mixed SAMs that were 50% hydroxylated.\textsuperscript{12} Folkers et al. studied the influence of chain length of mixed SAMs and discovered that large contact angle hysteresis exists when significant disorder occurs between the monolayer and the contacting liquid.\textsuperscript{13} Additionally, in mixed short/long-chain SAMs, a larger hysteresis was found when the longer chain was terminated with a polar group (-OH) and the shorter chain with a nonpolar group (-CH\textsubscript{3}). These studies indicated that the contact angle hysteresis is influenced by the surface roughness at the molecular level.

We have recently demonstrated that organic monolayers can be used as model systems to understand the evaporation phenomenon; our preliminary experiments showed the presence of two distinct evaporation modes for water droplets on mixed SAMs on gold.\textsuperscript{8} On these mixed alkanethiolate SAMs of approximately the same chain length, the effects of surface roughness are minimized.\textsuperscript{12,14} By varying the ratio of polar (-OH) and nonpolar (-CH\textsubscript{3}) groups in the SAMs, the surface energy (hydrophobicity/hydrophilicity) can be easily tuned. We have found that the evaporation mode switching is independent of surface hydrophobicity but correlates with the wetting hysteresis in the previous study.\textsuperscript{8} The present study extends these investigations to mixed monolayers (i.e., -OH- and -CH\textsubscript{3}-terminated) of different chain lengths on gold surfaces to investigate the effect of roughness at the molecular level of the surface interface. For generalization, other conventional solid materials, specifically Teflon, silicon wafers, and polycarbonate, were also examined.
3.2 Experimental Section

Gold substrates (regular glass slides first covered with 10-nm Cr, followed by 100-nm Au) were purchased from Evaporated Metal Films (EMF) Inc. (Ithaca, NY); 11-mercapto-1-undecanol (97%), 1-octanethiol (98.5+%), 1-decanethiol (96%), and 1-octadecanethiol (98%) from Aldrich; silicon (111) wafers (n-type) from Virginia Semiconductor, Inc. (Fredericksburg, VA); poly(tetrafluoroethylene) (Teflon) sheets from the local machine shop; and polycarbonate bases of CDs from Millennium Compact Disk Industries, Inc. (Vancouver, BC). Deionized water (>18.3 M\(\Omega\) was produced from a Barnstead EasyPure UV/UF compact water system (Dubuque, IA).

The silicon wafers and Teflon were cleaned by immersion in "piranha" solution (3:1 mixture of concentrated H\(_2\)SO\(_4\) and H\(_2\)O\(_2\) (30%)) for 30 min at 90 °C (CAUTION: use extreme care as piranha is explosive when in contact with organic materials), and then rinsed with deionized water. Gold slides were also cleaned in piranha solution but for a shorter period (5 min at 90 °C), followed by copious rinsing with water; they were then incubated in deposition solutions containing two thiols (11-mercapto-1-undecanol/1-octanethiol, 11-mercapto-1-undecanol/1-octadecanethiol, or 11-mercapto-1-undecanol/1-decanethiol) in 95% ethanol (total concentration 1.0 mM) for approximately 24 h at ambient conditions. It has been found by Bain et al. that there was no significant effect on the quality of the monolayers when the incubation time varies from overnight to two months.\(^{11}\) After removal from the deposition solution, the substrates were washed with ethanol and water sequentially and dried under nitrogen. Polycarbonate substrates were sonicated in ethanol for 10 min and rinsed with water.
A digital AST Optima contact angle apparatus with a horizontal light beam to illuminate the liquid droplet was used to monitor the evaporation process and measure the contact angles. Water microdroplets (1-5 µL with an uncertainty of less than 10%) were delivered to the substrates from automatic micropipettes. Analysis of the evaporation process under ambient conditions (temperature: 20 ± 3 °C, humidity: 30 ± 5%) was performed with software provided by the manufacturer. Droplets were monitored until they had completely evaporated. In practice, enlarged digital pictures of the droplet taken at 1-min intervals were fitted to the spherical-cap geometry in order to calculate the contact area, contact angle, and drop volume. In the range of 30-120° the precision was ±0.5°. However, the reproducibility of the measurements over different areas of the same sample (with different droplets) was only ±2°. The advancing and receding contact angles were measured by the method of Dettre and Johnson. In this method, decreasing the droplet volume until the point where the contact area decreases gives the receding contact angle (θ_r), and increasing the droplet volume until the point where the contact area increases gives the advancing contact angle (θ_a).

Atomic force microscopy (AFM) images were obtained from a custom-made instrument with a silicon nitride tip (Triangular D of MSCT-AUHW, Veeco Metrology group, resonance frequency 15 kHz, force constant 0.03 N/m). Areas of two different sizes (1 µm x 1 µm and 2 µm x 2 µm) were scanned in contact mode. AFM images were analyzed by calculating the root-mean-square (rms) roughness factor:

**Equation 3.1 - Root-mean-square roughness factor:**

\[
\sigma_{\text{rms}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (z_i - \bar{z})^2}
\]
3.3 Results

An understanding of how water microdroplets interact with solid surfaces and how the shape varies with time is essential for tuning the surface to have certain desired wetting properties. In our studies, the evaporation of water microdroplets from various substrates was followed by monitoring the contact angle, contact area, and drop volume as a function of time with the help of a digital contact angle apparatus. Mixed monolayers consisting of polar (-OH) and nonpolar (-CH₃) terminal groups of different chain lengths on gold were compared to determine if the evaporation modes are affected by the roughness at the molecular level along the interface of the solid.

We note that the composition for mixed SAM systems refers to the molar ratio in the deposition solution. It is well known that the solution is normally different from the actual composition of the SAM on the surface, which was confirmed previously by XPS studies. The data shows that there is preferential absorption for the -CH₃ terminated thiols onto the gold surface. This is also consistent with the estimation based on Cassie’s Equation (Equation 1.8).

Other conventional surfaces, such as Teflon, silicon wafer (a model system for semiconductor materials), and polycarbonate (a widely used polymeric substrate) that have totally different wetting properties and surface morphologies were also tested. The wetting hysteresis was measured subsequently on all surfaces and compared to the contact angle change during evaporation. AFM images were obtained to provide a better understanding of the correlation between the surface morphology and the evaporation process.
3.3.1 Mixed SAMs Prepared from Thiols of Different Chain Lengths.

Three binary SAMs consisting of the following alkanethiols in 1:1 molar ratios (in the deposition solution) were examined (Figure 3.1): (A) 1-octadecanethiol/11-mercapto-1-undecanol (C18/C11OH), (B) 1-decanethiol/11-mercapto-1-undecanol (C10/C11OH), and (C) 1-octanethiol/11-mercapto-1-undecanol (C8/C11OH). By maintaining the same substrate (gold films deposited on glass slides under vacuum), the underlying surface morphology is kept unchanged, and any variation in roughness is mainly a consequence of the different molecular lengths in the mixed monolayer.

![Figure 3.1: Schematic of the mixed SAMs on gold substrates.](image)
In Figure 3.2, we have shown the evaporation behaviour of water microdroplets on these model surfaces by monitoring the contact angle (A) and contact area (B), respectively, as a function of time.

Figure 3.2: Evaporation of water microdroplets from mixed SAMs on gold under ambient conditions. (A) Contact angle as a function of time. (B) Contact area as a function of time. Each mixed SAM consists of a 1:1 molar ratio of the two specified alkanethiols (in the deposition solution).
Although the molar ratio between polar and nonpolar groups remained the same for the three binary SAMs, their initial contact angles are different, presumably because of the different \( n \)-alkanethiol chain lengths. The \( \text{C}18/\text{C}11\text{OH} \) SAM is more hydrophobic than \( \text{C}10/\text{C}11\text{OH} \), which in turn is more hydrophobic than \( \text{C}8/\text{C}11\text{OH} \), since exposure of the longer chain termini to the wetting environment masks the effect of the functional group on the shorter chain.\(^{17}\) In all cases, when a water microdroplet was placed on the SAM surface, initially the contact angle decreased while the contact area remained constant. For \( \text{C}18/\text{C}11\text{OH} \) and \( \text{C}10/\text{C}11\text{OH} \) SAMs after approximately 5 min, the contact area began decreasing as the contact lines began to move inward (shrinking) while the contact angle remained constant. A similar trend was observed for \( \text{C}8/\text{C}11\text{OH} \); however, the switch to constant contact angle mode occurred after a longer period of about 10 min. No dependence has been observed on the water droplet volumes when they were kept relatively small (1-5 \( \mu \text{L} \)); however, the behaviour of larger droplets (>5 \( \mu \text{L} \)) is no longer dominated by surface tension effects as gravity begins to play a significant role.

The evaporation hysteresis (\( \Delta \theta_{\text{evap}} \)) is defined as the difference between the initial (\( \theta_i \)) and the "equilibrated" contact angle (\( \theta_e \)) (the constant angle reached after the initial decrease) that is extrapolated from the plot in Figure 3.2A. Although the three mixed SAMs show the same trend, they displayed distinct differences in the evaporation hysteresis, which are apparently sensitive to variations of the \( n \)-alkanethiol chain lengths. As shown in Table 3.1, \( \Delta \theta_{\text{evap}} \) for \( \text{C}8/\text{C}11\text{OH} \) is considerably larger than that for \( \text{C}10/\text{C}11\text{OH} \) and \( \text{C}18/\text{C}11\text{OH} \).
Table 3.1: Correlation between surface roughness, evaporation hysteresis, and directly measured wetting hysteresis. The root-mean-square (rms) roughness factor (AFM studies) is calculated for a 1 μm × 1 μm area. \(^a\) rms roughness factor for a 2 μm × 2 μm area. \(^b\) Directly measured difference between advancing and receding contact angles.

<table>
<thead>
<tr>
<th>Surface</th>
<th>rms roughness factor (Å)(^a)</th>
<th>rms roughness factor (Å)(^b)</th>
<th>Evaporation hysteresis (°)</th>
<th>Wetting hysteresis (°)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8/C11OH/Au</td>
<td>31.4</td>
<td>56.6</td>
<td>16.9 ± 2.0</td>
<td>16.6 ± 1.5</td>
</tr>
<tr>
<td>C10/C11OH/Au</td>
<td>---</td>
<td>---</td>
<td>9.5 ± 0.5</td>
<td>10.0 ± 0.4</td>
</tr>
<tr>
<td>C18/C11OH/Au</td>
<td>26.8</td>
<td>46.1</td>
<td>6.5 ± 2.8</td>
<td>7.0 ± 0.7</td>
</tr>
<tr>
<td>Teflon</td>
<td>138.2</td>
<td>---</td>
<td>19.4 ± 3.0</td>
<td>20.9 ± 3.2</td>
</tr>
<tr>
<td>Silicon oxide</td>
<td>24.6</td>
<td>46.4</td>
<td>10.0 ± 1.5</td>
<td>10.7 ± 2.8</td>
</tr>
<tr>
<td>polycarbonate</td>
<td>---</td>
<td>68.4</td>
<td>8.9 ± 2.0</td>
<td>10.0 ± 1.0</td>
</tr>
</tbody>
</table>

Figure 3.3: Contact mode AFM images of (A) C18/C11OH and (B) C8/C11OH SAMs on gold.
Direct measurements of wetting hysteresis ($\Delta \theta$), the difference between advancing ($\theta_A$) and receding ($\theta_R$) contact angles, using the method of Dettre and Johnson, were conducted on these surfaces for comparison. The results ($\Delta \theta = \theta_A - \theta_R$) agreed very well in magnitude with $\Delta \theta_{\text{evap}}$ (Table 3.1) for the three mixed SAMs. This finding is of significance because it confirms our hypothesis that the evaporation mode switching is dominated by the wetting hysteresis of the surface, as indicated previously on the mixed SAMs bearing molecules of the same alkyl chain lengths. It also demonstrates that one can accurately determine the wetting hysteresis from the evaporation trend of a liquid from a solid surface. The C18/C11OH surface was thought to be molecularly rougher due to the long C18 chains; therefore, a larger contact angle hysteresis would have been expected. In reality, a smaller evaporation hysteresis for the C18/C11OH surface was observed compared with the C8/C11OH system (Table 3.1). Folkers et al. have shown that for mixed short/long chain systems a larger wetting hysteresis is observed when the longer chain is terminated with a polar group (-OH). Our results may also be explained by the denser packing of mixed SAMs with long CH$_3$-terminated and short OH-terminated chains. Atre et al. have demonstrated that, in these mixed SAMs, adjacent long CH$_3$-terminated chains are organized in clusters and bend away from the shorter underlying OH-terminated chains, which may decrease the surface roughness at the molecular level. As a result, the surface roughness for mixed SAMs on gold is primarily determined by the topography of the underlying gold substrates, as verified subsequently by AFM studies. While the rolling hill topography expected for gold substrates (prepared by thermal evaporation) was observed, there is no significant difference between the two mixed monolayers (Figure 3.3). The $rms$
roughness factors were calculated for both a 2 \( \mu m \times 2 \mu m \) and a 1 \( \mu m \times 1 \mu m \) area and the trend in roughness compared for both cases (Table 3.1). The C18/C11OH system was indeed slightly smoother and had a smaller \textit{rms} roughness factor than the C8/C11OH system. This result correlates well with both the evaporation hysteresis and directly measured wetting hysteresis, suggesting that a rougher surface would have a larger wetting hysteresis.

Figure 3.4: Evaporation rate of water microdroplets from mixed SAM surfaces. (A) Drop volume (V) as function of evaporation time (t). (B) Linear relationship between \( V^{2/3} \) and \( t \).
Analyzing the evaporation rates of these systems, the volumes of the water microdroplets were found to decrease nonlinearly with time (Figure 3.4A); this indicates that the evaporation rates change as a function of time. According to the empirical model proposed by Rowan and Erbil based on the spherical drop assumption, $V^{2/3}$ versus $t$ plots are expected to be linear.\textsuperscript{20,21} In Figure 3.4B, we have shown that the evaporation of water from all three mixed SAMs does indeed follow this model. In addition, it can be concluded that the more hydrophilic a surface, the faster is the evaporation rate, which is consistent with our previous observations.\textsuperscript{8}

3.3.2 "Conventional" Substrates: Teflon, Polycarbonate, and Silicon Wafer.

To further elucidate the relationship between evaporation modes, wetting hysteresis, and surface roughness, experiments were conducted with the following three conventional substrates: (a) poly(tetrafluoroethylene) (Teflon), (b) silicon wafer, and (c) polycarbonate. Similar polymeric surfaces have been used in previous wetting and evaporation studies.\textsuperscript{1,3,4,22,23} Our evaporation studies revealed a trend similar to that of the mixed SAMs on gold (Figure 3.5), although the initial contact angles increased (from silicon wafer to polycarbonate to Teflon) as the hydrophobicity of the substrate increased.

The constant contact area mode (pinning) was first observed, and thereafter a switch to the constant contact angle mode (shrinking) occurred. Although the mode-switching trend was similar, distinct differences in the evaporation hysteresis, $\Delta \theta_{evap}$, were observed. As shown in Table 3.1, polycarbonate and silicon substrates exhibited much smaller $\Delta \theta_{evap}$ values than Teflon. More importantly, direct measurements of
wetting hysteresis compared very well to $\Delta\theta_{\text{evap}}$ with the Teflon substrate showing the largest value.

![Figure 3.5: Evaporation of water microdroplets from conventional substrates (Teflon, silicon, and polycarbonate) under ambient conditions. (A) Contact angle as a function of evaporation time. (B) Contact area as a function of time.](image)

The results for these three systems generalize our finding that the evaporation mode switching correlates with the wetting hysteresis of the surface and that evaporation plots can be used to evaluate the wetting hysteresis. Yet, clear differences among these
three substrates are noticeable. On relatively smooth surfaces, such as polycarbonate and silicon, the energy barrier impeding the movement of the solid-liquid-vapour three-phase contact line is small; therefore, the constant contact area mode does not dominate the course of evaporation. In this case, the switch to the constant contact angle mode occurs more readily, that is, during the first 5 min of evaporation (Figure 3.5). In contrast, on Teflon the constant contact area mode persists for a fairly long period of time (more than 10 min). This is due to a rougher surface pinning the contact line of a drop to a greater extent, that is, the drop sticks more tightly to the surface and must overcome a larger energy barrier to decrease its area.

The correlation between the mode-switching trend, specifically, the contact angle hysteresis (from both evaporation and direct measurements) and the roughness of the substrates were further evaluated by AFM topography studies (Figure 3.6). It appears that within a certain range of roughness the hysteresis values are similar, for example, approximately 10° for both polycarbonate and silicon wafers (although their \(\text{rms}\) roughness factors are slightly different). Because the latter were only cleaned in piranha solution without further treatments (for example, chemical etching in \(\text{NH}_4\text{F}\)), the surface had a thin silicon oxide layer that is not atomically flat. Therefore, the silicon samples showed a contact angle hysteresis comparable to that of polycarbonate and mixed SAMs on gold.

For Teflon the \(\text{rms}\) roughness factor is more than double those of the other two systems, and its wetting hysteresis is also considerably higher. These results agree with the previous finding that when the surface roughness increases, the contact angle hysteresis will increase accordingly. In addition, we believe that this high degree of
roughness for this particular brand of Teflon substrates is responsible for the observed high initial contact angle ($120^\circ$) in comparison to reported literature values of approximately $108^\circ$ for similar materials.\textsuperscript{26}

Figure 3.6: AFM images of conventional substrates: (A) polycarbonate base of CDs, \textit{rms}: 68.4 Å for a 2×2 μm area; (B) silicon wafers, \textit{rms}: 46.4 Å for a 2×2 μm area; and (C) Teflon sheets, \textit{rms}: 138.2 Å for a 1×1 μm area.
Figure 3.7: Evaporation rate of water microdroplets from conventional substrates. (A) Volume \( V \) as a function of evaporation time \( t \). (B) Linear relationship between \( V^{2/3} \) and \( t \).

The evaporation rates were also found to decrease non linearly with time in all cases (Figure 3.7). Similar to the mixed SAMs, a linear relationship was derived by plotting \( V^{2/3} \) versus \( t \) using the spherical drop assumption.\(^ {20,21} \) As the hydrophobicity of the surface increased (from silicon to polycarbonate to Teflon) the evaporation rate decreased, as indicated by the longer lifetime of the water microdroplets. The different
time scales for the entire evaporation process (i.e., 10 min for silicon wafers in comparison to 25 min for Teflon and polycarbonate) presented in Figures 3.4 and 3.7 may be due to the variability of the hydrophilicity of each substrate (different drop volumes were necessary to obtain stable droplets of a fairly symmetrical shape) and the atmospheric conditions (relative humidity and room temperature) that were not precisely controlled. While this certainly deserves further investigations, it is beyond the main focus (i.e., the evaporation modes / changing droplet shape, and the correlation with wetting properties) of this study.

3.4 Discussion

The present study substantiates that the evaporation mode switching is a direct manifestation of wetting hysteresis, as was confirmed for not only model SAM surfaces but also for conventional substrates. In conducting direct measurements of wetting hysteresis using the method of Dettre and Johnson (where the advancing angle is found by increasing the drop volume until the contact area begins to advance, and the receding angle by decreasing the drop volume until the contact area begins to decrease),\textsuperscript{15} we are essentially mimicking the process of evaporation where a droplet formed on a surface has an initial advancing front and, as evaporation proceeds, its volume decreases in constant contact area mode until the receding angle is attained. At this point, as evaporation causes the droplet volume to further decrease, the constant contact angle mode becomes dominant. This interpretation of evaporation, particularly its relation to surface roughness, is key to understanding the observations of other researchers who have noted results apparently different from ours. For example, Birdi and Vu observed only one mode for their substrates (glass and Teflon).\textsuperscript{3,4} Their results may be explained by examining the
very different surface topography of the two surfaces. For fairly rough surfaces, the contact line is pinned for a longer period, and the droplet may appear to evaporate in the constant contact area mode (decreasing angle). In this case, it is suggested that the receding contact angle $\theta_r$ has a value that is much smaller than the initial contact angle ($\theta_r \ll \theta_i$); therefore, a large hysteresis exists. Consequently, the switch to the constant contact angle mode may occur near the end of the evaporation process; depending on the increments of time measurements, this mode may be overlooked. Similarly, for smoother surfaces there is not much energy impeding the contact line; thus, the constant contact area mode may be easily missed because it is present for only a very short period during the initial stage of the evaporation (perhaps less than one minute), and the constant contact angle mode would appear to dominate the entire process. In this case, the receding angle is suggested to be close to the initial contact angle ($\theta_r \approx \theta_i$) and, as a result, the wetting hysteresis is approximately zero. Additional studies are warranted to confirm this hypothesis (for example, testing mixed SAMs on ultrasmooth gold surfaces$^9$), with the challenge arising from measuring the wetting hysteresis at the limits where only one evaporation mode is observed and very small time intervals (on the scale of one second or below) between measurements are needed.

Both chemical heterogeneity and surface roughness must be pondered before making generalizations about the dominant evaporation mode; it cannot be solely on the basis of whether a surface is hydrophobic or hydrophilic. Although it is not easy to unambiguously distinguish between the effects of surface roughness and chemical heterogeneity, we have shown that roughness plays a dominant role in the evaporation process on mixed SAMs on gold. In our previous study, the chemical heterogeneity of the
surface was changed by varying the OH component of the SAMs; the effects due to surface roughness were insignificant as similar alkyl chain lengths of polar (C11OH) and nonpolar components (C10) were used. We have found that varying the -OH content between 10 and 90% had no effect on the wetting hysteresis; a contact angle difference of approximately 10° always resulted, independent of the surface's hydrophobicity. This agrees with the results of Bain et al. who directly measured the hysteresis on mixed SAMs (C11/C11OH), and with the earlier work of Holmes-Farley et al. in which mixed monolayers formed from HS(CH2)15COOH and HS(CH2)15CH3 were tested with pH 3 water (to prevent ionization of the carboxy groups). Using ultrasmooth gold surfaces, Gupta et al. also demonstrated recently that surface chemical heterogeneity does not contribute to contact-angle hysteresis in mixed SAMs. It should be noted that the similar wetting hysteresis (10°) on the C10/C11OH monolayers corresponds to the inclusive mode switching from the initial constant contact area to the subsequent constant contact angle mode. Now we have shown that variations in roughness, even at the molecular scale, result in changes in the wetting hysteresis and, therefore, the timing for the evaporation mode switching. It is noted that this study is still limited in its ability to make a broad generalization of the evaporation phenomenon, as the experiments were carried out only under ambient conditions.

3.5 Conclusions

In examining the evaporation of water microdroplets from model SAM surfaces and conventional substrates (Teflon, polycarbonate, and silicon), an inclusive mode switching behaviour was observed. All surfaces exhibited an initial constant contact area mode and a subsequent constant contact angle mode. However, each surface showed a
distinct evaporation hysteresis, $\Delta \theta_{\text{evap}}$ (taken as the difference between the initial contact angle and the averaged angle in the constant contact angle regime). Furthermore, $\Delta \theta_{\text{evap}}$ was found to be consistent with the directly measured wetting hysteresis ($\Delta \theta = \theta_A - \theta_R$). This demonstrates that evaporation plots can be solely used as a simple and reliable means to evaluate the wetting hysteresis. Analysis of the evaporation rates for each system revealed that the volumes decreased nonlinearly; however, plots of $V^{2/3}$ versus $t$ showed a linear relationship. Generally, the more hydrophilic a surface, the faster is the evaporation rate. This study demonstrates that evaporation modes and rates are sensitive to changes in surface morphology on a scale as fine as the molecular level. It also shows that the data reported depend sensitively on the exact experimental conditions, thus rendering direct comparisons with literature observations difficult.

3.6 References

(8) Yu, H.-Z.; Soolaman, D. M.; Rowe, A. W.; Banks, J. T. *ChemPhysChem* 2004, 5, 1035-1038. (Note: XPS data along with studies on the difference between solution and surface compositions can be found in the supporting information).


CHAPTER 4: SURFACE MICROSTRUCTURE AND WETTING PROPERTY RELATIONSHIPS: CONTROLLED PATTERNING OF OXIDE THIN FILMS BY MONOLAYER-ASSISTED ELECTROCHEMICAL DEPOSITION\textsuperscript{1}

This chapter explores how surface morphology affects the wetting properties of a surface. The surface morphology of zirconia thin films are shown to be “tuneable” based on the variation of electrochemical parameters and the choice of substrates. Microcontact printing (μCP) was used to create “molecular templates” (patterned SAMs) on the surface; which in turn serve to guide the cathodic electrodeposition of zirconia thin films. The observed contact angles varied from 40° to 145° on these structurally tuneable oxide thin films, thus demonstrating the essential role of surface micro/nanostructure in controlling their wetting properties.

4.1 Introduction

The wetting property of a solid surface is closely related to two factors: 1) topographical structure (surface roughness) and 2) chemical heterogeneity (surface energy).\textsuperscript{1,2} As mentioned before, this is demonstrated by the Lotus leaf which has two roughness scales: micrometer bumps and nanometer hair-like features in addition to a wax layer that lowers it’s surface energy.\textsuperscript{1,3,4} There has been mounting interest in the scientific community to understand a surface’s chemical and structural relationship to

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wetting properties. It is well known that surface structure enhances water repellency considerably. The apparent contact angle on a roughened surface was described in Wenzel's theory where the liquid is assumed to fill the grooves of the roughened surface. For a rough surface where the droplet sits on fractional areas consisting of the solid surface and air, and does not fill the grooves, the modified Cassie's equation can be applied. These models which describe the influence of topography on minimizing the surface energy predict variations in contact angle as a function of surface roughness, suggesting a hydrophilic surface can be turned into a hydrophobic one by tuning it's roughness. In particular, Wenzel's equation predicts that enhancing the roughness of a surface will contribute to greater hydrophobicity only if the surface is initially hydrophobic. Therefore, according to this model a hydrophilic surface cannot be converted into a hydrophobic one by merely tuning its roughness, implying that this must be accompanied with a change in chemical composition of the surface. Thus, the conventional way of creating water-repellent surfaces has been to create rough structures on an already hydrophobic surface or by modifying a rough surface with compounds that will lower the surface energy, such as fluorinated groups. It is therefore of great interest to be able to create water repellency (without the use of waterproofing agents) by solely manipulating the structure of the surface. Of even greater significance is the ability to convert a hydrophilic surface into a hydrophobic surface while maintaining the same chemical composition, something not predicted by Wenzel's theory.

In the present work, electrochemical deposition along with the use of a monolayer template allows for the systematic study of the relationship between structure and wetting properties in a convenient and efficient manner. Microcontact printing (μCP) was used
to selectively modify a gold surface with alternating regions of \(-\text{CH}_3\) and/or \(-\text{OH}\) terminated alkanethiolate monolayers (Figure 4.1). We chose as our model system a zirconia film because of our previous work on this system and because these films have been well studied and characterized in the literature.\textsuperscript{11}

![Figure 4.1: (A) A PDMS stamp with 20-\(\mu\)m wide features (Stamp has 3 \(\mu\)m depth). (B) Patterning of a gold substrate with the stamp inked with octadecanethiol (C18) (1.0 mM, 95% ethanol). (C) Patterning of a gold substrate with C18 (\(\mu\)CP) and 6-mercapto-1-hexanol (C6OH) (deposition solution). (D) Electrochemical deposition of zirconia onto the C18-bare gold and C18-C6OH patterned gold substrates, respectively.](image)

4.2 Experimental Section

Octadecanethiol (98%) and 6-mercapto-1-hexanol (97%) were purchased from Aldrich (Milwaukee, WI). Ethanol (95%) was of ACS reagent grade and was used without further purification. Deionized water was obtained from a Barnstead EasyPure UV/UF compact water system (Dubuque, IA) with a resistance of 18.3 M\(\Omega\). Gold slides (first coated with 10 nm Cr followed by 100 nm Au) were purchased from Evaporated Metal Films Inc. (Ithaca, NY). Patterned polydimethylsiloxane (PDMS) stamps (Dow
Corning Corp., Midland, MI), for microcontact printing (μCP) were made by curing a 10:1 mixture of elastomer-hardener over lithographic silicon master templates.

Gold slides were cleaned with “piranha” solution (3:1 mixture of concentrated H₂SO₄ and 30% H₂O₂) for 5 min at 90° to remove organic contaminants (CAUTION: use extreme care as piranha solution is explosive when in contact with organic materials). The substrates were patterned with the desired alkanethiolate SAMs using μCP. PDMS stamps patterned with 20 μm stripes were “inked” with 1 mM solution of 1-octadecanethiol (C₁₈) in 95% ethanol and dried under nitrogen. The gold surface was then stamped on for ~30 seconds. When it was desirable to have alternating stripes of CH₃ and OH-terminated SAMs, after being patterned with the CH₃ monolayer the gold substrate was placed in a solution of 6-mercapto-1-hexanol (C₆OH, 1.0 mM, in 95% ethanol) for ~30 min then dried under nitrogen.

In our electrochemical measurements, the working electrode was the gold substrate, the counter electrode was a Pt wire, and the reference electrode was a AglAgCl|3 M NaCl. Electrochemical deposition was conducted with an Autolab Electrochemical Analyzer (PGSTAT30, Eco Chemie BV, Netherlands) in a faraday cage. The gold chip was pressed against the bottom of a Teflon cell using an O-ring seal, exposing an area of 0.69 cm². Zirconia films were formed from a solution of 5.0 mM ZrOCl₂·8H₂O and 0.1 M KCl in deionized water. Scan rates of 40 mV/s and 20 mV/s are presented here, the numbers of cycles was varied, and scan ranges of +0.8V to −1.2V was used. After deposition the films were dried under nitrogen gas. The films were then stored under ambient conditions for approximately one week to allow for complete and slow drying.
Wetting measurements on the prepared zirconia films were performed using a digital AST Optima contact angle apparatus with a horizontal light beam to illuminate the water droplet. Water droplet volumes of approximately 1.5 to 2.0 μL were delivered to the surface with micropipettes (having an uncertainty of less than 10%) to measure the contact angles. To analyze the surface morphology of the films, atomic force microscopy (AFM) images were obtained from a Topometrix Explorer AFM (8 μm-Z-Linearized scanner) using silicon nitride tips (Triangular D of MSCT-AUHW, Veeco Metrology group, resonance frequency 15 kHz, force constant 0.03 N/m). Images were acquired in contact mode and analyzed using Thermomicroscopes SPM Lab Software from which the root-mean-square (rms) roughness was calculated. Scanning electron microscopy (SEM) images were obtained from a FEI DualBeam Strata 235. Electrochemically prepared ZrO₂ films were imaged using secondary electron imaging (SEI) and grounded using carbon paste to avert charging of the sample. Typical accelerating voltages of 10 kV and magnification of ×5000 was used. X-ray photoelectron spectroscopy (XPS) was conducted on the electrodeposited zirconia films using a Perkin Elmer PHI 5400 ESCA System using Al Kα x-rays having an energy of 1486.6 eV.

4.3 Results and Discussion

4.3.1 Formation of the Molecular Template

In this study, we are exploring the application of patterned SAMs as molecular templates to control the electrochemical deposition of oxide thin films and to selectively alter their surface morphology, while maintaining the same chemical composition. For this purpose, gold slides were patterned with stripes of CH₃-terminated SAMs using μCP; these gold slides could be modified with alternating regions of CH₃ and OH-terminated
SAMs by placing the CH₃ monolayer-patterned slides in a deposition solution of OH-terminated thiol (Figure 4.1).

![Image](image_url)

**Figure 4.2:** (A) SEM image of a gold substrate patterned with stripes of C18 SAM. The areas of contrasting colour indicate a difference in conductivity between the two regions (5 μm stamp). (B) Lateral Force AFM image of a gold substrate patterned with C18 and C60H monolayers in stripes of equal spacing (10 μm stamp). The contrasting lines indicate the different force between the AFM tip and the functional groups in the C60H and C18 region.

In Figure 4.2A, the SEM image of a gold substrate patterned with alternating microstripes of a C18 SAM and bare gold shows clear contrast. This is due to the difference in conductivity since the region patterned with the C18 monolayer is less conductive. When the substrate is patterned with alternating stripes of two different SAMs, the contrast is not clear since the entire substrate is covered with organic monolayers and has relatively the same conductivity. However, these surfaces can be imaged with AFM operated under lateral force mode (Figure 4.2B). The contrasting stripes of equal dimensions indicate the difference in the frictional force between the terminal groups (CH₃ vs. OH) of the SAM and the AFM tip. Therefore, we believe that
our substrates are indeed patterned with the respective monolayers according to the dimensions of the PDMS stamp.

### 4.3.2 Electrochemical Deposition of the Oxide Thin Films

![Cyclic Voltammetric response of a gold cathode modified with patterned alkanethiolate monolayers under cathodic electrodeposition of a zirconia thin film (5mM ZrOCl₂·8H₂O and 0.1M KCl in deionized water). A scan rate of 40 mV/s and scan range of +0.8 to -1.1 V was used. The first and last scans show a decrease in the current due to the film becoming increasingly resistant to the redox process.](image)

Figure 4.3: Cyclic Voltammetric response of a gold cathode modified with patterned alkanethiolate monolayers under cathodic electrodeposition of a zirconia thin film (5mM ZrOCl₂·8H₂O and 0.1M KCl in deionized water). A scan rate of 40 mV/s and scan range of +0.8 to -1.1 V was used. The first and last scans show a decrease in the current due to the film becoming increasingly resistant to the redox process.

A zirconia film was then prepared on the surface using electrochemical deposition in a dilute solution of ZrOCl₂ at different scan rates to examine if the monolayer template can guide the deposition of the zirconia film. Figure 4.3 shows the typical CVs for the electrochemical deposition of ZrO₂ thin films, which did vary significantly when the surface is modified with patterned monolayers. The only clear change is that the peak
current drops upon repeated cycling, which is a result of the film becoming increasingly resistant to the redox process. The cathodic electrodeposition of zirconia onto gold substrates is an irreversible redox process as is seen in the cyclic voltammogram. Two irreversible peaks believed to arise from the complex redox behaviour of ZrOCl₂ on gold are observed at approximately −0.95 V and −1.05 V.¹¹

It is widely accepted that electrochemical deposition of oxide thin films (e.g., ZrO₂) involves the generation of base (OH⁻) at the cathode surface (gold).¹² The electrogenerated base can then hydrolyze metal ions or complexes, leading to the accumulation of colloidal particles near the electrode and the subsequent formation of the cathodic deposit. In the case of a zirconyl chloride salt, initially the salt dissociates, followed by hydrolysis of the zirconyl ion and the interaction of the hydrated cation with OH⁻ ions.¹³ Thereafter, the zirconium oxide forms after dehydration and polycondensation:

Equation 4.2 - Formation of ZrO₂:

\[
\begin{align*}
\text{ZrOCl}_2 & \rightarrow \text{ZrO}^{2+} + 2\text{Cl}^- \\
\text{ZrO}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Zr(OH)}_2^{2+} \\
\text{Zr(OH)}_2^{2+} + 2\text{OH}^- & \rightarrow \text{Zr(OH)}_4 \\
\text{Zr(OH)}_4 & \rightarrow \text{ZrO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

Nevertheless, the mechanism for the formation of zirconia is not well understood.¹⁴⁻¹⁶ Zirconia thin films formed from low temperature deposition methods are typically amorphous, having a cracked mud appearance due to the non-uniform contraction of the wet coating on drying.¹²,¹³
Figure 4.4: XPS data for the zirconia film prepared via cathodic electrochemical deposition. The characteristic 3d spin orbit components $3d_{5/2}$ and $3d_{3/2}$ for zirconia are observed.

Figure 4.5: Zirconia thin films electrochemically deposited on a gold substrate patterned with C18 SAM in 20 μm stripes. The bottom plot shows the cross section along the dashed line.
The SAMs act as a resist to block electrochemical deposition, allowing deposition to occur on the bare gold regions where base can be cathodically generated to form ZrO₂. Thus by patterning the SAMs on the surface it is possible to confine the growth of the zirconia film to selective areas and thus tune the surface morphology. These films were first characterized by x-ray photoelectron spectroscopy (XPS) (Figure 4.4). XPS data confirmed the formation of zirconia on the gold substrate by electrodeposition. The 3d peaks are characteristic of fully oxidized zirconium in the 4+ state and represent a splitting into two spin orbital components 3d_{5/2} and 3d_{3/2} having energies at 182.4 eV and 185.6 eV, respectively. After fitting our data and taking into account the relative shift in the carbon peak due to static charge our data compares well to the literature value for zirconia.

At a relatively fast scan rate (40 mV/s) there is pronounced confinement of the film to regions of bare gold. The electrochemical parameters were also found to play a substantial role in the type of film being formed. It was found that to obtain confinement of the zirconia film, optimal conditions are scanning from +0.8V to −1.1V since going more negative results in loss of confinement, thicker films, and substantial hydrogen evolution. Moreover, confinement was only observed at scan rates of 40 mV/s or greater, while slower scan rates resulted in no confinement. It was also found that the C18 monolayer gave the best results for confinement of this film, as the monolayer prepared from a long-chain alkanethiol exhibits better blocking effects on the cathode surface in comparison to shorter chain thiols. In Figure 4.5 the AFM analysis along with the line profile, shows clear confinement of the film along the stripes of bare gold, having heights
of approximately 200 nm. Slight deposition along the stripes blocked with C18 also occurred due to defects within the monolayer;\textsuperscript{19} nevertheless, deposition is highly favoured along the bare cathode regions.

![Figure 4.6: Zirconia thin films electrochemically deposited on a gold substrate patterned with C18 and C6OH SAMs in alternating stripes of 20 μm. The cross section of the AFM image along the dashed line is shown at the bottom.](image)

For the CH\textsubscript{3}/OH systems, very interesting results were found. For these systems the entire gold substrate is covered with a passivating layer of a monolayer C18/C6OH; therefore, cathodic generation of base is significantly hindered. However, there are limited regions where the cathode surface is not blocked by the monolayer such as at defects in the monolayer or pinholes. Interestingly, we observed that at high scan rates (>

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40 mV/s), a different pattern is observed in comparison to the C18-bare gold system. The C18/C6OH system displays a greater periodicity of confinement than the C18/bare gold system, having similar “mountain/valley” features (compare Figure 4.5 and 4.6). This is seen in the AFM image of Figure 4.6, where zirconia is confined to 5μm stripes having a height of approximately 400 nm. This type of confinement was only observed using two thiol molecules of different “heights”, such as in the C18/C6OH system. The reason for this difference in pattern is not yet understood: there are a few possibilities that lead to these results such as deposition may be more favourable at interfaces of the mixed SAMs. Differences in applied pressure to the stamps during μCP may also contribute to the differences. Also, when the substrate patterned with C18 is placed in the C60H deposition solution, spreading and diffusion of the methyl terminated SAMs may alter the pattern of the molecules on the surface, which in turn would affect the subsequent deposition confinement.

4.3.3 Correlation between Film Morphology and Wetting Properties

Varying the electrochemical parameters resulted in the formation of distinct film morphologies that demonstrate different wetting properties. The contact angle measurement on the C18-bare gold surface deposited with zirconia was found to be 115 ± 3° (Figure 4.7A) for 10 scans at 40 mV/s. For gold substrates patterned C18/C6OH, under similar deposition conditions, a contact angle of 110 ± 2° is observed (Figure 4.7B), similar to the C18/bare gold system.

The molecular template for both these systems helps to tune the surface morphology and significantly increase the hydrophobicity of the film. In comparison, a bare gold substrate (not modified with a molecular template) when deposited with a
zirconia film is very hydrophilic with a contact angle $< 40^\circ$. This is because the zirconia film is inherently hydrophilic due to the surface being hydroxyl terminated. FT-IR analysis along with deuterium exchange studies have confirmed that the surface of these films is hydroxyl terminated having large absorption bands in the $-\text{OH}$ region.\textsuperscript{20-22} Therefore, these results are remarkable, since a hydroxyl terminated surface has been converted into a hydrophobic one (without apparent changes in the chemical heterogeneity of the surface) via manipulation of the surface morphology only. Also, it should be noted, the zirconia thin films need to be left to dry in ambient conditions for approximately one week prior to wetting studies. Due to the fact that these films were formed in aqueous media, water droplets may enter the spaces between the nanostructures and be trapped. When the contact angle of these films was measured immediately after deposition, the films were found to be initially very hydrophilic, at times completely wetting the surface. However, after being left in ambient conditions to dry for at least one week, we believe the slow drying process or possible condensation reactions allow for the enhanced roughening/texturing of the surface allowing for the subsequent hydrophobic behaviour. Thereafter, these films sustained their hydrophobic property after being wetted numerous times while conducting contact angle measurements.

At the slower scan rate of 20 mV/s there is a significant loss of film confinement on the gold substrates patterned with stripes of C18 SAMs. We believe at these slow scan rates, there is more time for diffusion-controlled processes to occur. For systems patterned with alternating stripes of $-\text{CH}_3$ terminated SAMs, 20 mV/s results in the deposition of larger particles (Figure 4.7C). Therefore, the “mountain/valley” features
are no longer visible, which results in a decrease in the surface roughness. To create thicker films a scan range of +0.8V to −1.2V was used. Water droplets placed on these systems wet the surface and have contact angles of around 40°.

Figure 4.7: (A) Atomic Force imaging of zirconia films deposited on SAM-patterned gold substrates. Inset: Contact Angle measurements for each film. (A) C18/bare gold: 10 scans at 40 mV/s, 115° (B) C18-C6OH: 10 scans at 40 mV/s, 100° (C) C18/bare gold: 15 scans at 20 mV/s, 40° (D) C18-C6OH: 15 scans at 20 mV/s, 145°.

When the substrate was patterned with both CH₃ and OH-terminated SAMs in alternating stripes (the C18/C6OH system) and scanned at 20 mV/s for 15 scans the film was found to drastically improve its hydrophobicity into the near superhydrophobic region
with a contact angle of 145° (Figure 4.7D). Due to the slower scan rates, there is a loss of apparent confinement (i.e., no significant height difference). Nevertheless, the underlying template still acts to affect the resulting film morphology. Two different features are clearly visible with these films, with the interface between the two SAMs having larger “cracks”. This water-repellent behaviour is understood from AFM analysis where two distinctly patterned morphologies on the microscopic scale are observed in the film, and on the finer scale the nanometer bumps on the surface that are reminiscent of the features of the Lotus leaf.\(^3\)\(^,\)\(^4\) We believe that both these roughness scales play a significant role in enhancing the hydrophobicity of the inherently hydrophilic zirconia film. The vast increase in contact angle was achieved simply by increasing the roughness of the surface without any further chemical modification of the film.

This observation of making an inherently hydrophilic material into a hydrophobic one cannot be described by Wenzel’s equation, since according to this equation there are limitations for a wetted hydrophilic surface to become hydrophobic by simply changing the roughness factor \(r\). Therefore, for the roughened hydrophobic surfaces, they must follow Cassie’s Law for a composite surface since Wenzel’s equation does not hold for non-wetting surfaces.\(^23\) That is, the droplet sits on fractions of air and solid and does not intrude into the bumps on the surface. Therefore, although the surface of the film may be terminated with hydrophilic (OH) groups, the chemical nature of the film does not seem to play a dominant role in dictating the wetting properties in some cases (as seen here). Rather, the roughness of the film, which has the ability to support the droplet on a composite surface of air and substrate, contributes significantly to the superhydrophobic behaviour. Extrand has found that certain parameters must be met for creating water-
repellent surfaces. He notes that in most cases a liquid deposited on a rough surface will spread and engulf surface asperities; however when the drop is suspended on top of surface asperities and air pockets, this gives rise to extremely large contact angles of 140 to 180° characteristic of super-repellent surfaces. Furthermore, three conditions must be met for a surface to demonstrate water-repellent behaviour: 1) the interaction of the liquid with the surface features must direct forces at the contact line upwards; 2) the surface forces must be large enough to support the liquid against the downward pull of gravity; and 3) the surface features must be tall enough that liquid protruding does not contact the underlying solid. We believe that these criteria are met in our zirconia films deposited on the C18/C60OH systems, which demonstrates water repellent behaviour with a contact angle close to 150°, the generally accepted “threshold” for superhydrophobicity.

To study the dependence of the contact angle on the electrochemical parameters (number of scans and scan rates, which eventually changes the thickness and roughness of the thus formed thin films), two systems were studied (Figure 4.8). Gold substrates were modified with C18 patterned in 20 µm stripes and zirconia was deposited at either 20 mV/s or 40 mV/s while the number of scans was varied. For the systems scanned at a rate of 20 mV/s the scan range was from +0.8V to -1.2V, which allowed for thicker films to form on the surface, whereas the systems scanned at a rate of 40 mV/s were scanned in a range of +0.8V to -1.1V, allowing for formation of thinner films. It is clearly seen from the graph that there is a clear effect of the electrochemical parameters on the water contact angles. At 40 mV/s as the number of cycles increased from 5 to 10, the contact angle increases: the zirconia film could be tuned from 95° (for 5 cycles) to a hydrophobic 121° (for 10 cycles).
The increase in roughness was monitored with AFM where the root mean square roughness (\textit{rms}) was calculated (See Chapter 3, Equation 3.1). At 5 scans the \textit{rms} is 7.27 nm, whereas at 10 scans the \textit{rms} value increases to 121.7 nm (\textit{rms} values were found by scanning over a 50 × 50\textmu m area). However, it was found that as the number of cycles continued to increase, the film became noticeably smoother. This was due to a loss of confinement and the “mountain/valley” morphology as the film builds up. Evidence of this is seen with the decrease in contact angle in addition to the decrease of the roughness. Similarly, with the systems scanned at 20 mV/s, going from 5 scans to 10 scans the contact angle increases from 100° to 114°. This increase in contact angle can be correlated to the increase in roughness of the film with the \textit{rms} values of the films being...
56.9 nm and 215.9 nm respectively. Thereafter, as the film continues to build up, the surface becomes smoother as the effect of the molecular template is lost; this is similarly reflected by a decrease in the roughness. Although the \( \text{rms} \) values give a good indication of the average roughness of the surface which increases the hydrophobicity, the surface morphology with its unique micro/nanostructure play a greater role in dictating the wetting properties. Thus a unique contact angle is not observed on a surface with a given \( \text{rms} \) value since the contact angle will be significantly influenced by the specific surface features (information that is not obtained by the \( \text{rms} \) value).

In these systems of the C18/bare gold, higher contact angles were achievable scanning at 40 mV/s compared to 20 mV/s, since at the faster scan rate there is more pronounced confinement of the film leading to a more roughened surface. For comparison, experiments were conducted where zirconia was deposited on bare gold electrodes at scan rates of both 20 mV/s and 40 mV/s. The films formed were very hydrophilic, having contact angles of approximately 30° or less. Furthermore, as more scans were conducted, the films became more and more hydrophilic. This trend is opposite to the films formed using the molecular templates, where as more scans were run the film would increase its hydrophobicity. As a result, it is clear that the molecular templates play a large role in guiding the deposition of these zirconia films to create surfaces with roughened features. Furthermore, having these special surface features is necessary for creating films with increasing hydrophobicity.

### 4.4 Conclusion

We have shown that superhydrophobicity could be achieved simply by an increase in the surface roughness. By using an inherently hydrophilic film and varying
the roughness through electrochemical deposition it is possible to make such films water-repellent without further chemical modification. Although the Lotus leaf and other water-repellent materials are known to owe their behaviour to both surface roughness (bumpy epidermal cells of the plants) and chemical nature (waxy cuticles), there is much to be learned from exclusively modifying the surface by varying just one of these parameters. This would help to establish certain limits such as the roughness scales needed for hydrophobicity. Work is in progress in our group to understand such trends and limits in terms of surface roughness and chemical heterogeneity.

4.5 References


CHAPTER 5: CONCLUSION

5.1 Concluding Remarks

The wetting and evaporation behaviour of microdroplets on molecularly modified substrates have been investigated in this thesis. Specifically, examination of three main factors: 1) the liquid’s composition 2) the interface and 3) the substrate morphology, led to insightful observations that has helped us come closer to understanding these ubiquitous phenomena in nature. By investigating whether the wetting/evaporation behaviour observed for pure substances could be generalized to other systems, we studied the evaporation of binary liquids, in which similar modes of evaporation such as constant contact angle and constant contact area were observed; however, the evaporation profile differed with an additional stage that is closely related to the evaporation of the volatile component (Chapter 2).

It has been shown that the surface morphology plays a dominant role in influencing wetting and evaporation behaviour (Chapter 3). We have found that the wetting hysteresis is dependant on the surface roughness even at a molecular level (evidenced by using mixed SAMs prepared from thiols of different chain lengths).

In studying the effect of substrate morphology on wetting properties, it was found that the hydrophobicity of the surface could be tuned simply by controlling the surface features (Chapter 4). Using electrochemical deposition on patterned SAMs (as molecular templates), zirconia thin films can be selectively deposited at desired locations. It is
remarkable that this inherently hydrophilic metal oxide could be made to have a range of wetting properties, i.e., from hydrophilic to superhydrophobic.

5.2 Future Work

Wetting property of a surface is not a trivial phenomenon, and there is still much to be learned. In order to understand how a liquid will interact with a surface many factors must be considered and evaluated systematically. The work in this thesis has shown that simple generalizations such as those made in the past concerning the wetting and evaporation behaviour of certain liquids and substrates cannot be easily made. We have recently found that for certain compositions of propanol-water mixtures on gold surfaces modified with hydrophobic decanethiol SAMs, a “non-evaporating” droplet results. This is marked by the unusually slow evaporation time scale of hours that differs remarkably from the time scales of liquid evaporation studied thus far, which is on the time scale of seconds or minutes. We believe that these extremely long evaporation times can be attributed to a concentration gradient brought on by the hydrophobic substrate with a higher concentration of the alcohol near the substrate. As a result, after the initial increase in contact angle to the new equilibrium position, the non-evaporation mode sets in. This may be attributed to a strong hydrogen-bonding network that forms among the water molecules at the top of the droplet, which prevents the movement of alcohol molecules to the surface. However, further studies are needed to model this non-evaporation phenomenon in order to gain a better understanding of how liquid composition affects wetting.

To further understand how substrate morphology affects wetting, further investigations are needed. Having surface patterning with an even greater control will
allow for a more systematic study. The limitations of the roughness scale and the chemical composition that affect wetting would offer a great insight into how to exploit the two main parameters that influence wetting. In the future, of interest would be to study the evaporation profile water microdroplets on the metal-oxide films with different morphologies. It would be useful to evaluate how the evaporation profiles differ as the hydrophobicity of the zirconia film is changed. In order to make generalizations into the wetting properties that occur for the evaporation of pure liquids, more experiments are also needed on other substrate materials having a range of wetting properties from superhydrophobic to superhydrophilic. This would help to answer the question as to whether the mode switching (from constant contact area to constant contact angle) is correlated to the wetting hysteresis in all cases, even on the superhydrophobic surfaces.

A better knowledge into the wetting phenomena will allow for a greater control of surface properties and has the potential for technological applications. By understanding the relationship between surface morphology / chemical modification and wetting properties, these factors can be further exploited to create surfaces with a desired wetting property, from superhydrophilic to superhydrophobic.

5.3 References