

Evaporation of Microdroplets of Ethanol–Water Mixtures on Gold Surfaces Modified with Self-Assembled Monolayers

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The wetting property and evaporation behavior 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 a preliminary 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” behavior 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.

Introduction

It has been proven that the wetting properties of a surface are important from both fundamental and technological perspectives,^{1,2} and that they are naturally related to the understanding of evaporation phenomena of liquid droplets from solid surfaces. Our previous studies demonstrated the possibility of using molecularly tailored surfaces, such as gold substrates modified with alkanethiolate self-assembled monolayers (SAMs), to study fundamental aspects of wetting property and evaporation behavior of sessile microdroplets and, particularly, their correlation with one another.^{3,4} This novel approach not only provides more control of the chemical composition of a surface but also permits the researchers to readily alternate the wetting property of a surface to investigate any possible variations in the evaporation profile.³ In retrospect, evaporation studies have traditionally been done on pure substances, and models have often been proposed to understand the significance of changes in two important parameters that dictate the wetting/evaporation of a liquid microdroplet on a solid surface: contact angle and contact area (or radius). In this paper, we endeavor to explain the three distinct stages observed in the evaporation process of a binary system (ethanol–water mixture) and determine how these parameters (contact angle and contact area) play a role in dictating the behavior of binary systems.

The first account of a scientific study of evaporation rate was done by Hedestrand more than 80 years ago.⁵ Briefly, he tried to evaluate the influence of an organic film on the surface to the evaporation rate of water; however, this pioneer work was later criticized by two other researchers who insisted that stagnant air directly above the water surface had a much more prominent effect on the evaporation rate than the substrate itself.^{6,7} Thereafter, 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.

In 1977, Picknett and Bexon monitored the changes in mass and constructed an experimental profile of a microdroplet of methylacetate evaporating on a poly(tetrafluoro)ethylene (Teflon) surface.⁸ They observed two evaporation modes: *constant contact angle* with decreasing contact area, and *constant contact area* with decreasing contact angle. They occasionally saw a “switch” between the two aforementioned modes of evaporation, which they believed was governed by wetting hysteresis, the difference in the advancing and receding angles of a microdroplet on a surface. In the early 1990s, Birdi and Vu explored the correlation between surface wetting properties and their effects on evaporation behavior of water microdroplets.^{9,10} For an initial contact angle $< 90^\circ$, they noted that the evaporation rate was linear and the contact radius constant. For an initial contact angle $> 90^\circ$, they noted that the evaporation was nonlinear, the contact angle constant, and the contact radius decreased.¹⁰ Thereafter, several research groups have intensively studied the evaporation behavior of sessile microdroplets both experimentally and theoretically;^{11–20} however, 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.^{3,4} We have documented at least three advantages with using these systems: (1) the molecules in the monolayer are closely packed in a highly oriented fashion;²¹ (2) the SAMs introduce controlled chemical heterogeneity at the interfaces; and (3) wetting properties can be tuned by altering the composition of the mixed monolayers.^{22,23} 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).³ We have experimentally confirmed that the “sudden” switch between the two modes is governed by the wetting hysteresis. Recently, we

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have extended these investigations to mixed monolayers of different chain lengths along with conventional solid materials (silicon wafer, plastics, and glass slides) for comparison.⁴

Herein, we use these model substrates (i.e., gold surfaces modified with SAMs) to explore the evaporation behavior of microdroplets of binary mixtures, a topic that has not yet been thoroughly investigated.^{24,25} Rowan et al. pioneered the evaporation studies of 1-propanol/water mixtures on poly(methyl methacrylate) in 2000.²⁴ 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 behavior of ethanol–water mixtures on a rough Teflon surface and proposed a three-stage “model” to describe the entire process.²⁵ 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.⁴ 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.

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 ($>18.3 \text{ M}\Omega\cdot\text{cm}$) 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_2SO_4 and 30% H_2O_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_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 $2.0 \pm 0.3 \mu\text{L}$ from various ethanol concentrations were delivered to the modified gold substrates using micropipets and were allowed to completely evaporate under ambient conditions ($22.7 \pm 1.5^\circ\text{C}$ with relative humidity of 40–50%). Enlarged optical images were taken by using the manufacture software in 1 min intervals; however, 30 or 15 s intervals were also used if a more accurate qualitative graphical depiction of the data was required.

Results and Discussion

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 vapor phases.²⁶ 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.¹¹ In the present study, microdroplets of

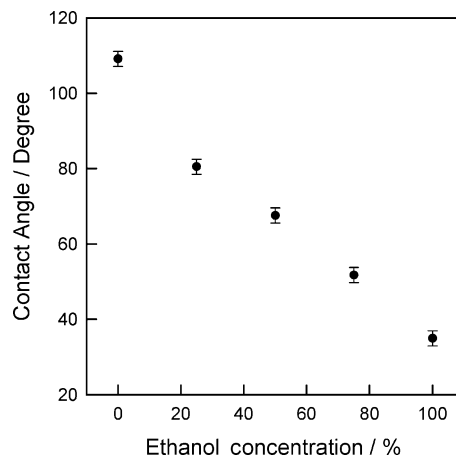


Figure 1. Plot of initial contact angles of microdroplets of ethanol–water mixtures on gold surfaces modified with 1-decanethiolate SAMs.

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 1, the initial contact angle of the microdroplet decreased from 109 ± 2 to $35 \pm 2^\circ$ as the concentration of ethanol increased from 0 to 100% (vol %). Due to the hydrophobicity of the surface ($-\text{CH}_3$ terminated),^{3,21–23} such a trend is naturally predicted since it is favorable for ethanol molecules to “wet” the surface. Ethanol has a vapor pressure higher than that of water at room temperature;²⁷ therefore, the surface of the droplet and surrounding vapor 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 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,^{3,4} it was shown that the evaporation of water microdroplets follows an inclusive trend, that is, from pinning (decrease in contact angle accompanied by constant contact area) to shrinking (constant contact angle accompanied by a linear decrease in contact area). We proposed that this sudden switch in the evaporation mode is governed by the wetting hysteresis,^{3,4} that is, the difference between the advancing and receding contact angles (i.e., $\Delta\theta = \theta_{\text{adv}} - \theta_{\text{rec}}$), which can be directly determined by the method of Detre and Johnson.²⁸ 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/ethanol; as shown in Figures 2 and 3 (black lines and the insets), the evaporation process shows an apparent switching between the pinning and shrinking modes, and the difference between initial and equilibrated contact angles

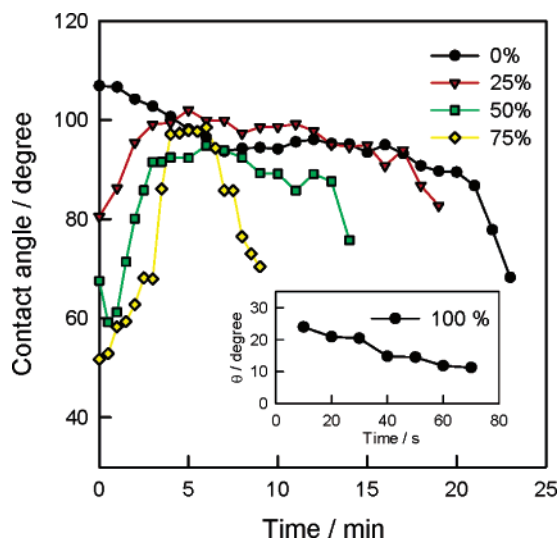


Figure 2. Plot of contact angles as a function of time for the evaporation of microdroplets of ethanol–water mixtures on SAM-modified gold surfaces.

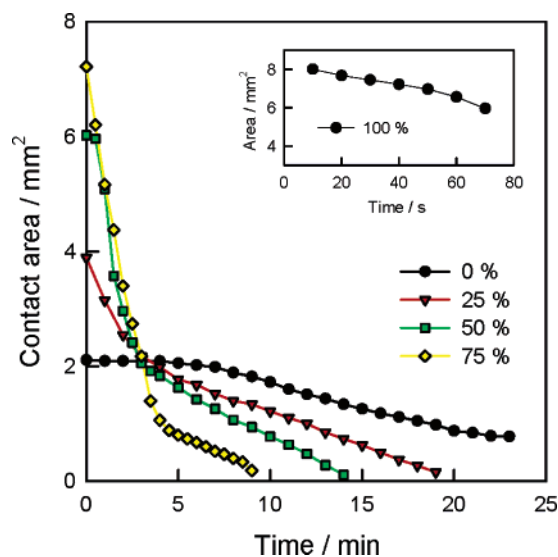


Figure 3. Plot of contact area as a function of evaporation time for the microdroplets of ethanol–water mixtures on gold surfaces modified with 1-decanethiolate SAMs.

is about 10° (although the time scale for the two liquids differs significantly from each other). 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 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 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/vapor 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 vapor phase), leaving behind a droplet that becomes increasingly rich with the less volatile compo-

nent.²⁷ 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, 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.²⁴ 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).²⁷

A close look at the initial contact angle increase phase of the evaporation curves (shown in Figure 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). This instability of the 50% mixture may be understood by the two competing effects resulting in either a local maximum or local minimum in the surface tension.²⁴ At this composition, both components are present in equal amounts; therefore, at the surface of the droplet, there are likely patches of ethanol and water. It is believed that the ethanol patches result in a local minimum in the surface tension; however, at the same time, the surface of the droplet is undergoing evaporative cooling resulting in a surface tension local maximum. The competition between these effects results in an instability of the droplet contact line, and this may contribute to an initial decrease in the contact angle before it increases to a maximum. The other feature in Figure 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.

As shown in Figure 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). In all cases, two stages are observed for 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 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 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.

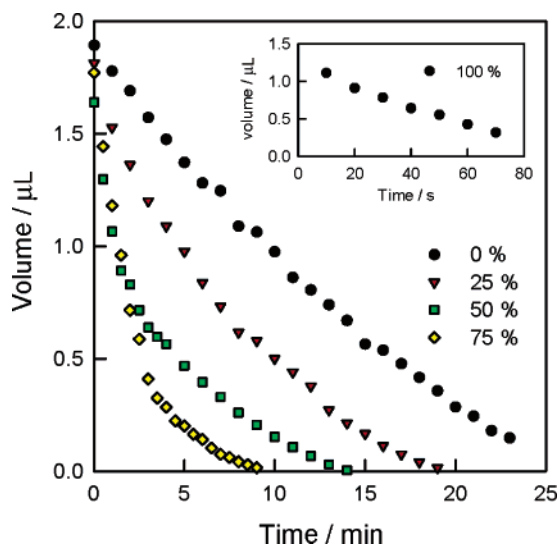
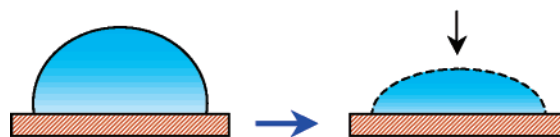


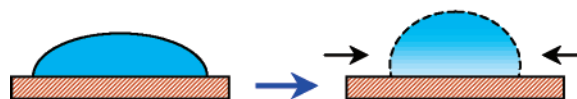
Figure 4. Plot of volume as a function of evaporation time for the microdroplets of ethanol–water mixtures on gold surfaces modified with 1-decanethiolate SAMs.

Droplet volume versus unit time was also plotted for all five solutions (Figure 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 vapor 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.²⁹ 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.^{29,30} They have suggested that the fast evaporation rates of the more volatile component can result in nonisothermal behavior in which the surface undergoes a decrease in temperature in comparison to the interior as the droplet undergoes evaporative cooling.³⁰ 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 vapor 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 vapor 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 vapor pressure in comparison to that of ethanol. This observed change in evaporation rate with time is indicative of an unsteady-state evaporation process in compari-

Mode 1: Pinning



Mode 2: Evaporating



Mode 3: Shrinking

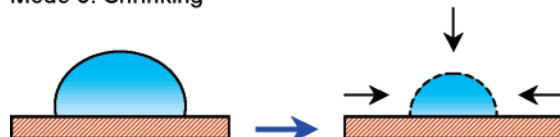


Figure 5. Three distinct modes in the evaporation behavior of ethanol–water mixtures on SAM-modified gold surfaces. See text for details.

son with steady-state evaporation processes where evaporation rate is constant with time.²⁹ It should be interesting to analyze these experimental data of binary systems with the model proposed by Erbil and co-workers on pure liquid systems,^{15–16,31} for which further investigations are currently underway.

Sefiane et al. proposed a three-stage model to explain the evaporation behavior of ethanol–water solutions on a poly-(tetrafluoro)ethylene (Teflon) surface.²⁵ 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).⁴ Herein, we can further elaborate and simplify the three-stage (mode) evaporation process as depicted in Figure 5, which deviates but closely correlates to the two modes observed for the pure water system reported previously.³ 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 (which relates to the aforementioned structural instability of the microdroplets on the surface). 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 behavior of pure water microdroplets observed previously.³ In this case, the contact angle remains relatively constant, but the contact area decreases linearly.

Unlike 1-propanol/water mixtures,²⁴ 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 4, inset), which makes the contact angle measurements practically difficult.

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, 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, 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.^{32–33}

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Supporting Information Available: Figures of evaporation of microdroplets of ethanol/water and 1-propanol/water mixtures on Au SAMs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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