"Non-Evaporating" Microdroplets on Self-Assembled Monolayer Surfaces under Ambient Conditions

Alan K. H. Cheng, Dinah M. Soolaman, and Hua-Zhong Yu*

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

Received: December 31, 2006; In Final Form: May 1, 2007

A unique "non-evaporation" phenomenon, i.e., the unusually slow evaporation process of sessile microdroplets on self-assembled monolayer (SAM) surfaces, is reported. It has been observed that only droplets containing a certain proportion of a volatile and a less-volatile component undergo non-evaporation, which is characterized by hours-long existence of the droplets maintaining constant contact angle, contact area, and volume. We propose that for alcohol–water binary mixtures on SAM surfaces, the highly orientated and closely packed hydrophobic 1-decanethiol molecules induce a concentration gradient of alcohol in water, with a higher concentration of alcohol near the SAM surface. Initial evaporation of the alcohol (more volatile) increased the contact angle until the establishment of a new composition, which contains a strong hydrogen-bonding network among the water molecules in the presence of the alcohol alkyl chains. There is a lessened tendency for the alcohol to evaporate in the presence of a concentration gradient due to such interactions, which results in the observed "non-evaporating" phenomenon. This type of unusual evaporating profile was not observed on conventional substrates, such as polycarbonate sheets and microscope glass slides modified with alkyltrichlorosilanes.

Introduction

Many research groups around the world have laid the foundation for understanding the evaporation of sessile microdroplets from solid surfaces by studying rates of volume changes and by proposing schematics to model the shape variations.[1–12] Our initial contribution to this research was to study water microdroplets on gold surfaces modified with self-assembled monolayers (SAMs).[13] The work expanded on principles related to wetting properties of the substrate and showed that the evaporation profile is solely dependent on the droplet composition rather than the surface hydrophobicity. Although roughening or pillaring of the surface may affect the surface's wetting properties, we have proved experimentally that the difference between the equilibrium contact angle and the initial contact angle of the evaporation profile is an accurate estimation of wetting hysteresis (difference between the advancing and receding contact angles) measured directly by the conventional method of Dettre and Johnson.[14] Taking advantages of the controlled composition and wetting properties of mixed SAMs on gold,[13] we have shown that the evaporation of pure substances follows an inclusive "pinning" (decreasing contact angle, constant contact area) to "shrinking" (decreasing contact area, constant contact angle) trend. This finding was further validated on mixed SAMs with different alkyl chain lengths and other conventional substrates (silicon and polymeric materials).[15]

We then proceeded to consider the evaporation of multicomponent systems, which are of practical importance, for example, in the fabrication of DNA microarrays via robotic spotting.[16] We found that in the evaporation of a binary liquid mixture on a hydrophobic surface (i.e., gold modified with n-alkanethiolate SAMs), a more complex profile has been observed.[17] The initial

"pinning" (constant contact area, decreasing contact angle) is due to the evaporation hysteresis; the subsequent "evaporating" mode (increasing contact angle, decreasing contact area) is due to evaporation of the more volatile species (e.g., ethanol in ethanol–water mixtures); the final "shrinking" mode (decreasing contact angle, decreasing contact area) is due to the final consumption of the droplet and evaporation of the remaining nonvolatile species (e.g., water in ethanol–water mixtures). This finding is in general agreement with that reported previously by Sefiane et al.[18] and Rowan et al.[19] on different polymeric surfaces.

Very few studies, however, have been performed on extremely slow evaporating ("non-evaporating") sessile droplets: it is intuitive that the evaporation rate of liquid droplets is dependent on the vapor content of the surrounding atmosphere. Yekta-Fard and Pointer[20] as well as Kamusewitz et al.[21] have investigated this phenomenon by monitoring the contact angle of droplets in the presence of different concentrations of surrounding vapor. Recently, Shanahan addressed the question of whether a sessile drop in an atmosphere saturated with its vapor is really at equilibrium:[22] for sessile droplets in highly saturated conditions, the evaporation time could theoretically be in the order of 15 days, neglecting the effect of ambient convection currents and slight temperature variations. It was also noted that even in conditions with 100% saturation of the vapor content, the droplet will inevitably evaporate.[22]

Beverley et al. have considered the alteration of evaporation rates by either encasing liquid droplets in microstructures such as porous solids and emulsions, or passing a controlled gas flow above the droplet during evaporation.[23] They proposed that evaporation can be rate-limited by three possible reasons. First, the stagnant gas layer above the droplet can be rate limiting. Second, a significant energy barrier may be present that prevents the leaving and entering of molecules from the liquid/vapor interface. Third, evaporation of a more volatile component from

---

* To whom correspondence should be addressed. E-mail: hzyu@sfu.ca.

a binary mixture sets up a concentration gradient in the droplet, so subsequent mass transfer within the droplet is rate limiting. The first two reasons are generally applicable, while the latter is only suitable for the evaporation of binary or multicomponent systems.

An equally probable reason that could explain a long evaporation time exhibited by certain binary mixtures is intermolecular interactions. Alcohol−water mixtures, for example, are miscible because of strong intermolecular hydrogen bonding.[24] There are four types of hydrogen bonds possible in alcohol−water mixtures: water−water; alcohol−alcohol; excess water−alcohol; and excess alcohol−water. Mizuno et al.[24−26] studied the hydrogen bonding interactions of ethanol−water system with ^{1}H NMR. They showed that, using the methyl protons of ethanol as a reference, the chemical shift of the water proton moves continuously to a lower field up to ethanol concentrations of approximately 8% (mole fraction), then to a higher field with further increase in ethanol concentration.[24] The initial shift to low field is interpreted as the strengthening of hydrogen bonding in among water molecules (the first of the four types of hydrogen bonds aforementioned) in the presence of ethanolic alkyl groups. The subsequent high field shift for higher ethanol concentrations can be interpreted as the depolarization of water molecules as the hydrophobicity of the system increases due to the presence of increasingly more ethanol molecules. The significance of this "maximum" in the chemical shift of the water proton in increasing concentrations of ethanol can be interpreted as the highest strength of water hydrogen bonding interactions possible in the system, hence it can be postulated that this "strength" prevents droplet evaporation.

In this paper, we endeavor to describe our unexpected observation of "non-evaporating" behavior of microdroplets on SAM surfaces under ambient conditions, i.e., an unusual evaporation profile of sessile droplets containing 1-propanol−water mixture at ambient conditions, which keeps constant contact angle, contact area, and droplet volume for a prolonged duration. Without the aid of atmospheric saturation, such non-evaporating droplets exhibit a lifetime of approximately 5 h. This is substantially longer than that reported in the literature,[1−12,13,15,17−19] which normally exhibits an evaporation duration from seconds to tens of minutes.

Experimental Section

Gold substrates (glass slides first coated with 5-nm Cr, followed by 100-nm Au) were purchased from Evaporated Metal Films, Inc. (Ithaca, NY), regular glass slides from Premiere, polycarbonate bases of CDs from Millennium Compact Disk Industries, Inc. (Vancouver, BC), 1-decanethiol (96%) from Aldrich, and hexadecyltrichlorosilane (95%) from Fluka. Deionized water (>18.3 Ω cm) was produced from a Barnstead EasyPure UV/UF compact water system (Dubuque, IA) and 1-propanol purchased from Commercial Alcohols Inc. (Brampton, ON).

The gold slides were treated with "piranha" solution (3:1 mixture of concentrated H_2SO_4 and 30% H_2O_2) for 5 min at 90 °C, followed by a rinse with copious amounts of deionized water. The cleaned gold plates were incubated in 1 mM 1-decanethiol solution in 95% ethanol for 24−48 h, then subsequently washed with 95% ethanol and dried with N_2. It has been shown by Bain et al.[27] that there is little effect on the quality of the monolayer when the incubation time varies from overnight to months. 1-Propanol−water mixtures of different concentrations were prepared with absolute 1-propanol and deionized water. Microscope glass substrates were cleaned in

"piranha" at 90 °C for 1 h; after rinsing with copious amounts of deionized water, they were incubated in 1 mM hexadecyltrichlorosilane/toluene for 24−48 h for surface modification. After removal of the substrate from the deposition solution, it was washed thoroughly with the solvents and dried with N_2. Polycarbonate sheets (cut from a CD base) were washed by sonication in absolute ethanol for 10 min, rinsed with water then dried with N_2.

Surface tension was measured with the du Noüy ring method. Briefly, a Pt/Ir ring was submerged into 1-propanol−water mixtures of various concentrations and then slowly lifted up. The force required to detach the ring from the liquid surface was measured, which is proportional to the surface tension of the solution. Between successive measurements, the ring was washed with benzene and rinsed thoroughly with butanone, and then the ring was flamed with a Bunsen burner until it appeared orange-red in color.

A digital AST Optima contact-angle apparatus (AST Products, Inc., Billerica, MA) was used to monitor the evaporation process of liquid microdroplets on SAM surfaces. Microdroplets of various 1-propanol−water concentrations with volumes 1.2 to 2.0 μL were delivered to the substrates using calibrated micropipettes and allowed to completely evaporate under ambient conditions (23.0 ± 2.0 C° and relative humidity of 25−35%). In each trial of the evaporation studies, the variation of relative humidity was within 2%. Enlarged optical images were taken at different time intervals; the corresponding contact angle, contact area, and drop volume were obtained based on a fit to a spherical cap shape with the software provided by the manufacturer. More specifically, the VCA Optima[TM] software (v. 1.71) was used to determine these parameters; i.e., five markers (L, R, T, 1, 2) are placed around the circumference of the droplet for calculating the contact angle, contact area, and the droplet volume after capturing an image. The obtained drop dimensions (in particular the volume) were calibrated against a calibrated micropipette using pure water with the aid of an analytical balance.

Results

As part of our systematic study on wetting and evaporation properties of multicomponent microdroplets on SAM surfaces,[13,15,17] the phenomenon of "non-evaporation" was observed unexpectedly with a 1-propanol−water mixture. Of all tested mixtures with different concentrations of 1-propanol in water, the only concentration that exhibited a significant non-evaporation behavior was 60/40 (1-propanol/water; v/v): a 1.0 to 1.5 μL droplet did not evaporate until 5 h after the droplet was deposited on the SAM surface (Figure 1A). Other 1-propanol-water mixtures of varied concentrations (e.g., 10/90) evaporated within minutes (Figure 1B), which is in agreement with that reported by Rowan et al. on a poly(methyl methacrylate) surface.[19] It was previously observed that the droplet volume change for pure liquids and alcohol−water mixtures is a monotonic, nonlinear decrease from the initial volume to zero.[13,15,17] As shown in Figure 1A, non-evaporating droplets show an unique droplet volume change profile that are "multifeature"−that is, it exhibits several "regions" in which the droplet volume either decreases or is essentially constant. It is remarkable that 60/40 1-propanol-water droplets exhibited such a unique behavior (Figure 1A) while other concentrations (for example, 10/90 as shown in Figure 1B) did not. The origins of multiple features in the volume−time profile of the 60/40 mixture will be elaborated in a further discussion of the overall scheme (i.e., contact angle and contact area changes) of the non-evaporation process.
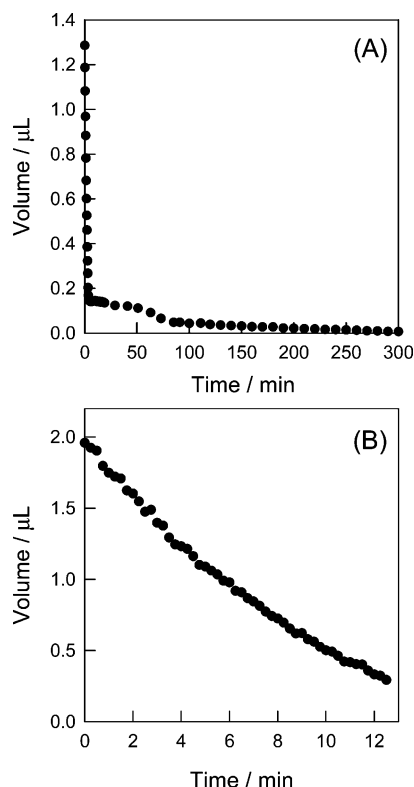
"Non-Evaporating" Microdroplets

J. Phys. Chem. B, Vol. 111, No. 26, 2007 **7563**

Figure 1. Plots of volume as function of time for binary microdroplets (A) 60/40 and (B) 10/90 (1-propanol/water; v/v) on gold surfaces modified with 1-decanethiolate SAMs.

To shed light on the unique evaporation behavior at certain concentrations, the initial contact angles (taken within 5 s of the droplet being deposited on the surface) of 1-propanol−water mixtures on SAM surfaces were measured (Figure 2A). Due to the hydrophobic nature of the surface (modification with 1-decanethiols),[13,27−29] it is predicted that the contact angle should decrease as the concentration of 1-propanol increases. Although the 0/100 solution (pure water) had the largest contact angle and the 100/0 (pure 1-propanol) had the smallest, an unusual "regional" maximum in contact angles is observed for the 60/40 1-propanol-water mixture. This is perhaps indicative that the wetting property of 60/40 mixture on SAM surface is not solely determined by the surface tension (i.e., contact angles are defined by Young's equation);[30] it may be also influenced by other physical/chemical properties of the droplet at that composition that have not been considered before. We have further examined other compositions near the 60/40 mixture (insert in Figure 2A), which confirmed the existence of such a local maximum at this particular composition. In an attempt to resolve the apparent disagreement between Young's equation and the contact angle−concentration profile, direct surface tension measurements on all the mixtures were carried out. As shown in Figure 2B, the surface tension shows a decrease as the proportion of 1-propanol increases in the binary mixture; no local maximum in the surface tension-concentration plot was observed. This suggests that the abnormality in Figure 2A was not a result of the surface tension. This was further confirmed with two additional contact angle-concentration plots of these binary mixtures on other substrates: microscope glass slides modified with hexadecyltrichlorosilanes (Figure 3A) and polycarbonate plates (Figure 3B). The contact angle profile of modified glass slides showed no local maximum for the 60/40 mixture; no data were available for polycarbonate, since when concentrations are higher than 25% of 1-propanol, the droplet
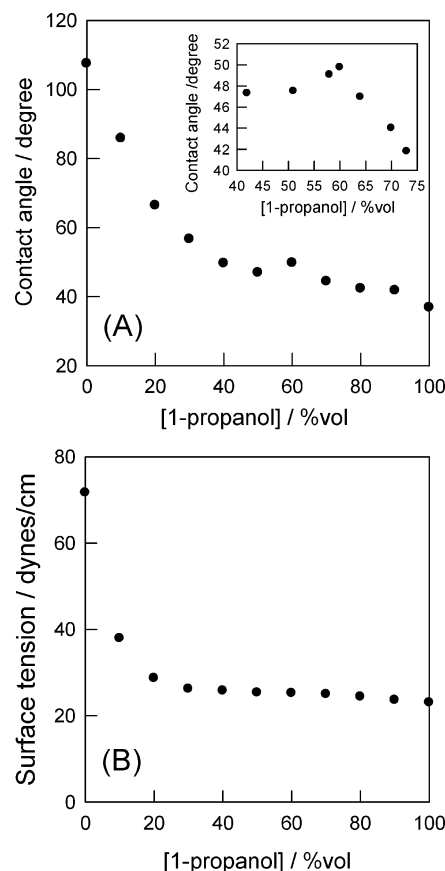

Figure 2. (A) Initial contact angle of 1-propanol−water microdroplets on gold surfaces modified with 1-decanethiolate SAMs; (B) Surface tensions of 1-propanol−water solutions determined by the du Noüy ring method.

completely wets the surface, thus rendering the surface incompatible for contact angle measurements. It is important to note that 1-propanol−water mixtures of all compositions did not undergo a prolonged evaporation process on these two substrates. These results confirmed that abnormalities in the evaporation profile for 60/40 1-propanol on SAM surfaces was governed by not only surface tension of the solution, but also the substrate (or modifications of the substrate) on which the mixture evaporates—which aspects of the substrate (roughness,[15] structural patterning, chemical heterogeneity etc.) that govern the phenomenon has not been evaluated before.

Figure 4 depicts the contact angle change as a function of time for the evaporation of 60/40 1-propanol-water microdroplets on SAM-modified gold surfaces. Figure 4A shows the first 6 min of the evaporation process: the initial decrease in the contact angle signifies the evaporation hysteresis, which follows the first mode in the inclusive three-stage evaporation trend observed previously for ethanol−water microdroplets.[17] We are convinced that other binary alcohol−water systems are akin in their evaporation behavior to the ethanol−water system described previously.[17−19] In Figure 4B, which depicts the contact angle change as function of time throughout the entire duration of evaporation, an increase in the contact angle is evident from approximately 50 to 100 min. This is in accordance with the second mode in the three-stage trend, which refers to the evaporation of the more volatile component (in this case, 1-propanol). It is important to note that this increase in the contact angle took approximately 100 min, but for ethanol−water systems, this increase in contact angle takes less than 3 min.[17] Already, it is notable that there is somewhat stability within the droplet (starting around 3 min in the evaporation
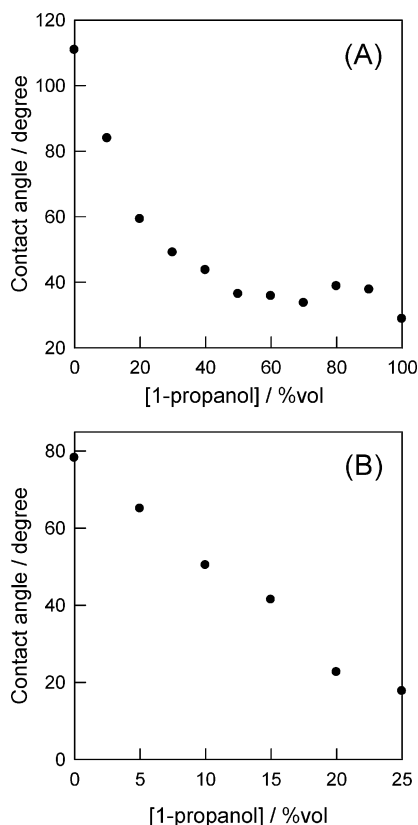
Figure 3. Contact angle of 1-propanol−water microdroplets as function of alcohol concentration on (A) microscope glass slides modified with hexadecyltrichlorosilanes and (B) polycarbonate plates.
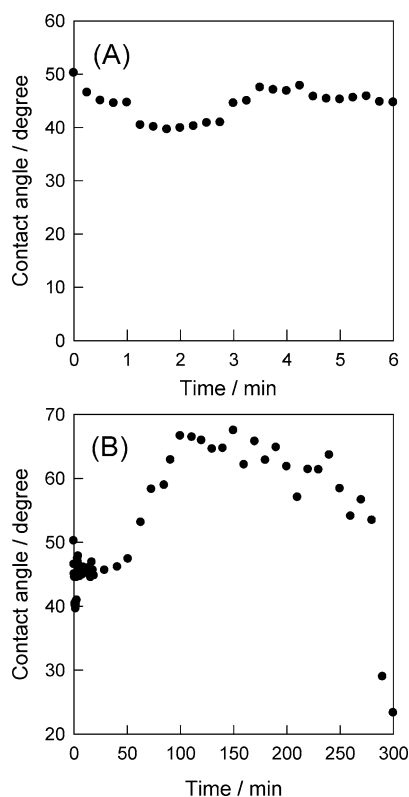

Figure 4. Contact angle of 1-propanol−water microdroplets (60/40, v/v) as function of time on 1-decanethiolate SAM surface: (A) from 0 to 6 min; (B) from 0 to 300 min.

process) that accounts for an unusually slow switching from mode I to II. The evaporation behavior may be dependent on the changes of 1-propanol/water ratio in the droplet as it comes
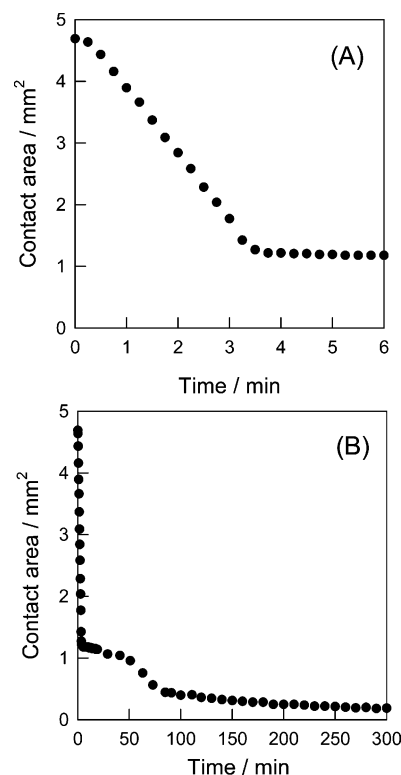

Figure 5. Contact area of 1-propanol−water microdroplets (60/40, v/v) as function of time on 1-decanethiolate SAM surface: (A) from 0 to 6 min; (B) from 0 to 300 min.

close to azeotropic composition (i.e., 0.4 mole fraction of 1-propanol, approximately 73.5% by volume of 1-propanol[31]). However, the 60/40 mixture is below azeotropic composition and it is intuitive that the proportion of 1-propanol should decrease as the evaporation occurs. On the other hand, the contact angle only increases to approximately 70°, which is below the "equilibrated" contact angle of 100° of the evaporation of pure water (0% alcohol) on the same type of SAM surface.[13,15,17] This differs from that observed for ethanol−water microdroplets where the contact angle increased to the "equilibrated" contact angle of the less volatile component (water). Starting from 100 min, we define the system as undergoing a "non-evaporation" mode. At the terminal stage of the evaporation process (after almost 5 h), the contact angle is shown to decrease abruptly. This is comparable to the third mode in the three-stage trend, which describes the final consumption of the droplet, and is not likely governed by any of the phenomena aforementioned.

Figure 5 depicts the evolution of the contact area as a function of time: the top plot (Figure 5A) shows the initial behavior of the droplet from 0 to 6 min. A brief "pinning" is observed in the first 15 s into the evaporation process followed by a linear decrease. At approximately 3 min, the contact area stayed constant and lasted until the 50 min (Figure 5B), where the contact area started to decrease. As noted before, this decrease in contact area is merely an accompaniment to the increase in contact angle due to the evaporation of the more volatile 1-propanol species from the droplet to the non-evaporation composition. The constant contact area from 100 to 300 min signifies "non-evaporation" behavior, until the terminal consumption of the droplet.

Discussion

Here it is useful to recall Lundgren and co-workers' work[32] and its relation to the present observation; they performed a
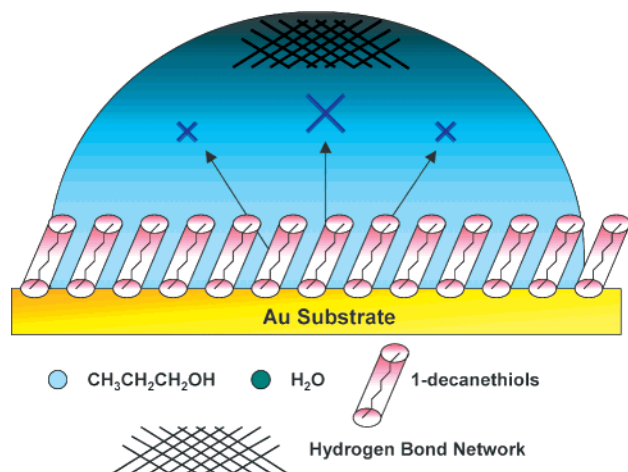
Figure 6. Hypothetic representation of "non-evaporating" 1-propanol–water microdroplets. On the hydrophobic SAM surface composed of highly ordered methyl-terminated alkyl chains, the less polar molecules (1-propanol) tend to aggregate near the surface of the substrate, while the more polar molecules (water) tend to aggregate near the surface of the droplet. At a specific final concentration distribution, the hydrogen bond network in water molecules is the strongest, and 1-propanol, which tends to evaporate due to its higher volatility, cannot evaporate easily since it has to pass the network of hydrogen bonds via mass transport. Water also does not evaporate quickly due to its lesser tendency to evaporate (as a result of the intermolecular hydrogen bonding). Ultimately neither component evaporates resulting in non-evaporation.

molecular dynamics simulation, with the ultimate goal of shedding light on the wetting behavior of ethanol–water droplets on a nonpolar (hydrophobic) graphite surface. Their system is comparable to the present 1-propanol–water system on hydrophobic SAM surfaces. They found that the tendency for ethanol molecules, over water molecules, to exist at the bottom of the droplet is higher. Thus, as the number of alcohol molecules deplete resulting from its evaporation (as it is more volatile) in binary alcohol–water systems, a concentration gradient is established, with the bottom of the droplet being alcohol rich and the top of the droplet being water rich. Mizuno et al.[26] showed that in the presence of alcoholic alkyl chains at a particular concentration, the water molecules in alcohol–water mixtures form maximally strong hydrogen bonding interactions, thus stabilizing the "network of water molecules" near the top of the droplet. This prevents alcohol molecules from migrating up; thus, mass transport of molecules from the bottom to the top of the droplet is rate-limiting,[26] which may eventually result in a prolonged evaporation profile (so-called non-evaporation). In the contact angle-time plot, starting from 3 to 50 min, the system is already unusually stable probably because the droplet is developing into a composition where water molecules are near maximum hydrogen-bonding capability. The increase in contact angle from 50 to 100 min signifies evaporation of the 1-propanol (more volatile) molecules; therefore, the contact angle increases to approximately 70°. However, the "equilibrated" contact angle of pure water on this SAM surface is above 100°, which suggests that the present system does not contain pure water (residual 1-propanol is present). At around 100 min until the end of the evaporation period, we predict that the composition of the droplet is one such that water molecules are in maximum hydrogen-bonding capacity at the top of the droplet, and hence 1-propanol molecules that are near the bottom of the droplet can hardly undergo mass transport to counteract the established concentration gradient (Figure 6). This could account for abnormally slow evaporation rates, thus leading to the apparent non-evaporation behavior.

As noted before, non-evaporation was observed on a gold surface modified with 1-decanethiolate SAM, but not on polycarbonate plates and microscope glass slides. It has been documented that for SAMs on gold, the molecules are in a highly oriented fashion and can be used to introduce chemical homogeneity/heterogeneity at the interfaces.[28] Despite their fragility (mechanically and thermally)[28,33−34] upon removal from the deposition solution, SAMs are homogeneous and are well-suited for novel applications involving topics that have not been sought, such as the phenomena of wetting and evaporation of microdroplets. In contrast, alkyltrichlorosilane-modified glass surfaces do not offer the same advantages as gold surfaces with alkanethiolate SAMs. Most notable is that although both systems offer controlled chemical modification of the surface, the quality of the monolayers on glass surfaces depends on subtle factors such as the water content in the system and reaction temperature, which should be optimized carefully.[28,35−36] For this reason, the SAMs on gold have gained broader acceptance; ultimately non-evaporation phenomena on these molecular films are evident. Most likely due to the close-packing and order of the hydrophobic molecules on surface, the SAM induces a concentration gradient in the microdroplets sitting on the surface as aforementioned (Figure 6). In the past, functionalized SAMs on gold have been shown to be able to control the oriented nucleation and growth of calcite,[37] and to drive the switching of liquid crystals.[38] We may also consider the selective adsorption of 1-propanol molecules on the SAM surface from the binary droplets, which would help to explain the apparent disagreement between Young's equation and the contact angle-concentration profiles (shown in Figure 1A) and the creation of concentration gradient of 1-propanol in the droplet that influences the overall evaporation behavior.

It should be pointed out that in this paper we do not endeavor to explain in detail why non-evaporation occurred solely on SAM surfaces, but assert that these molecular films are optimal for studying this phenomenon due to homogeneity of the alkanethiol molecules in a highly ordered fashion upon self-assembly. Nevertheless, we note that this work certainly deserves further discussions, particularly the microscopic origin of the "non-evaporation" phenomenon, for which more experimental investigations and theoretical modeling are warranted in our laboratory.

Conclusion

We have found a qualitative generalization on the evaporation of "non-evaporating" droplets on SAM surfaces: a droplet with a specific composition of a volatile and a less-volatile (usually polar) component is chosen such that upon evaporation of the volatile component, a new composition is made that maximizes the intermolecular interactions between molecules of the nonvolatile component. It has been proposed that on this hydrophobic SAM surface, the increased affinity between molecules of the nonvolatile component prevents the volatile species (located along the substrate surface) to undergo mass transfer and migration through the established concentration gradient. Thus, the nonvolatile species, which does not preferentially evaporate, stays at the surface of the droplet, while the volatile species cannot migrate through the strong intermolecular network of the nonvolatile species, which ultimately leads to the so-called non-evaporation behavior.

7566 *J. Phys. Chem. B, Vol. 111, No. 26, 2007*

Cheng et al.

References and Notes

(1) Picknett, R. G.; Bexon, R. *J. Colloid Interface Sci.* **1977**, *61*, 336–350.

(2) Birdi, K. S.; Vu, D. T.; Winter, A. *J. Phys. Chem.* **1989**, *93*, 3702–3703.

(3) Birdi, K. S.; Vu, D. T. *J. Adhes. Sci. Technol.* **1993**, *7*, 485–493.

(4) Bourgès-Monnier, C.; Shanahan, M. E. R. *Langmuir* **1995**, *11*, 2820–2829.

(5) Rowan, S. M.; Newton, M. I.; McHale, G. *J. Phys. Chem.* **1995**, *99*, 13268–13271.

(6) Erbil, H. Y.; Meric, R. A. *J. Phys. Chem. B* **1997**, *101*, 6867–6873.

(7) McHale, G.; Rowan, S. M.; Newton, M. I.; Banerjee, M. K. *J. Phys. Chem. B* **1998**, *102*, 1964–1967.

(8) Erbil, H. Y.; McHale, G.; Rowan, S. M.; Newton, M. I. *Langmuir* **1999**, *15*, 7378–7385.

(9) Erbil, H. Y.; McHale, G.; Newton, M. I. *Langmuir* **2002**, *18*, 2636–2641.

(10) Hu, H.; Larson, R. G. *J. Phys. Chem. B* **2002**, *106*, 1334–1344.

(11) Cachile, M.; Bénichou, O.; Poulard, C.; Cazabat, A. M. *Langmuir* **2002**, *18*, 8070–8078.

(12) Cachile, M.; Bénichou, O.; Cazabat, A. M. *Langmuir* **2002**, *18*, 7985–7990.

(13) Yu, H. Z.; Soolaman, D. M.; Rowe, A. W.; Banks, J. T. *ChemPhysChem* **2004**, *5*, 1035–1038.

(14) Dettre, R. H.; Johnson, R. E. *J. Phys. Chem.* **1965**, *69*, 1507–1515.

(15) Soolaman, D. M.; Yu, H. Z. *J. Phys. Chem. B* **2005**, *109*, 17967–17973.

(16) Dugas, V.; Broutin, J.; Souteyrand, E. *Langmuir* **2005**, *21*, 9130–9136 and references therein.

(17) Cheng, A. K. H.; Soolaman, D. M.; Yu, H. Z. *J. Phys. Chem. B.* **2006**, *110*, 11267–11271.

(18) Sefiane, K.; Tadrist, L.; Douglas, M. *Int. J. Heat Mass Transfer* **2003**, *46*, 4527–4534.

(19) Rowan, S. M.; Newton, M. I.; Driewer, F. W.; McHale, G. *J. Phys. Chem. B* **2000**, *104*, 8217–8220.

(20) Yekta-Fard, M.; Ponter, A. B. *J. Colloid Interface Sci.* **1988**, *126*, 134–140.

(21) Kamusewitz, H.; Possart, W.; Paul, D. *Int. J. Adhes. Adhes.* **1993**, *13*, 243–249.

(22) Shanahan, M. E. R. *Langmuir* **2002**, *18*, 7763–7765.

(23) Beverley, K. J.; Clint, J. H.; Fletcher, P. D. I. *Phys. Chem. Chem. Phys.* **2002**, *2*, 4173–4177.

(24) Mizuno, K.; Miyashita, Y.; Shindo, Y.; Ogawa, H. *J. Phys. Chem.* **1995**, *99*, 3225–3228 and references therein.

(25) Mizuno, K.; Oda, K.; Maeda, S.; Shindo, Y; Okumura, A. *J. Phys. Chem.* **1995**, *99*, 3056–3059.

(26) Mizuno, K.; Mabuchi, K.; Miyagawa, T.; Matsuda, Y.; Kita, S.; Kaida, M.; Shindo, Y. *J. Phys. Chem. A* **1997**, *101*, 1366–1369.

(27) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155–7164.

(28) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533–1554 and references therein.

(29) Semal, S.; Bauthier, C.; Voué, M.; Eynde, J. J. V.; Gouttebaron, R.; De Coninck, J. *J. Phys. Chem. B* **2000**, *104*, 6225–6232.

(30) Young, T. *Philos. Trans. R. Soc. London* **1805**, *95*, 65–87.

(31) National Research Council (U.S.). *International Critical Tables of Numerical Data*, *Physics*, *Chemistry and Technology*; McGraw-Hill: New York, 1933; Vol. 3, p 310.

(32) Lundgren, M.; Allan, N. L.; Cosgrove, T. *Langmuir* **2002**, *18*, 10462–10466.

(33) Nishida, N.; Hara, M.; Sasabe, H.; Knoll, W. *Jpn. J. Appl. Phys., Part I* **1996**, *35*, 5866–5872.

(34) Kluth, G. J.; Sung, M. M.; Maboudian, R. *Langmuir* **1997**, *13*, 3775–3780.

(35) Wang, R.; Wunder, S. *Langmuir* **2000**, *16*, 5008–5016.

(36) Vallant, T.; Brunner, H.; Mayer, U.; Hoffmann, H.; Leitner, T.; Resch, R.; Friedbacher, G. *J. Phys. Chem. B* **1998**, *102*, 7190–7197.

(37) Aizenberg, J.; Black, A. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 4500–4509.

(38) Luk, Y.-Y.; Abbott, N. L. *Science* **2003**, *301*, 623–626.