Autophobic Pinning of Drops of Alkanethiols on Gold[1]

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This paper establishes conditions necessary for autophobic pinning of solutions of alkanethiols by their reaction with a gold surface. Interfacial tension and the kinetics of organization of the SAMs are important considerations in the design of systems that limit the spread of drops across a surface that is reactive toward those drops. The two systems investigated in this paper—hexadecanethiol (HDT) spreading on gold in air and hydroxyundecanethiol (HHT) in hexadecane spreading on gold under water—provide a basis for understanding one aspect of the mechanism of microcontact printing (µCP) based on the reaction of thiols with bare gold. Adsorbates on the gold surface, and the roughness of the surface, ultimately limit the extent to which liquids are pinned on the surface of gold and constrain pinning of these liquids (and determine the resolution of patterning) by µCP and related methods.

Introduction

This paper describes qualitative studies of autophobic pinning of liquid solutions of alkanethiols on self-assembled monolayers (SAMs) of alkanethiolates on gold and outlines the importance of this phenomenon for microcontact pinning (µCP).[2-4] Many methyl-terminated SAMs are autophobic toward solutions with even relatively low surface tensions because the solid–vapor interfacial free energy of a surface composed of methyl groups (γ'_{sv}-(CH$_3$) ~ 18 erg/cm^2) is too low to support spreading of the solution. Surfaces exposing more polar groups—acids, hydroxyls, nitriles—are not autophobic, in air, to the solutions from which they are formed.

Placing and controlling the location of drops of thiols on gold constitutes the basis of techniques for forming patterns in the composition of SAMs by µCP and other techniques.[4-9] A central question in µCP concerns the sharpness of the boundaries of the region of SAM that is formed, and the influence of autophobicity on the edge resolution. Since formation of a SAM by reaction of an alkanethiol with bare gold is exothermic,[10] reactive spreading of liquid alkanethiol on the stamp might plausibly result in spreading SAMs far beyond the region of contact. It does not do so, when the procedure is properly carried out. Why not? In brief, the key issue is the autophobicity of the system (Figure 1). If the liquid wets the monolayer, reactive spreading will drive the drop edge far beyond the point of application. If the system is
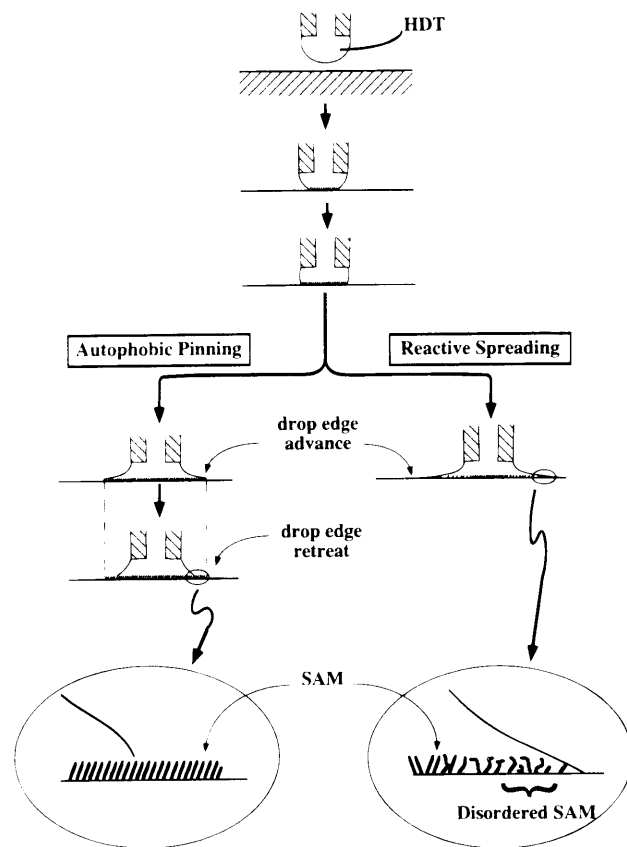
Figure 1. Schematic representation of a drop of HDT, and its spread, as the drop contacts a gold surface. The scheme contrasts two regimes: reactive spreading and autophobic pinning.

autophobic, the drop edge will spontaneously retract once the SAM has formed. The more rapidly an autophobic SAM forms, the sharper the edge might be expected to be.

Nomenclature

Autophobicity is a well documented phenomena:[4,11-19] a liquid in contact with a surface modifies the chemistry

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of this surface and lowers its solid–vapor and solid–liquid surface tension, and the liquid retracts spontaneously (Figure 1). Autophobic systems include many solutions of alkanoic acids on alumina or silica,[20,21] of long alkyl chain alcohols on zinc oxide,[16] and of alkyl siloxanes on silica.[18] **"Reactive spreading"** across a surface describes the forward movement of liquid caused by its reaction with the surface, and the spread of this liquid as a film over the modified surface. The contact angle of the leading edge of the drop of reacting liquid with the modified surface is low when reactive spreading occurs. **"Reactive Autophobic spreading"** describes the process by which a drop of liquid moves spontaneously across a surface, forming an autophobic SAM as it moves. Although the contact angle at the leading edge of this drop is low because it is reacting with the surface, the contact angle of the trailing edge of the drop—where the SAM has already formed—is high. This dynamic difference in contact angles causes spontaneous movement of the liquid as a drop (see below). We apply the term **"autophobic pinning"** to situations in which an autophobic liquid generates an autophobic surface by reaction and in which the liquid remains a drop and does *not* spread. Both leading and trailing edges of these drops have high and approximately equal contact angles with the surface (Figure 1). We call these drops "pinned".

Although Young's equation (eq 1)[11] describes an equilibrium

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \qquad (1)$$

system where no net force exists on the line of contact between liquid, surface, and air, we have also found it a useful starting approximation in considering the complex, nonequilibrium, dynamic phenomena that are the subject of this paper. When reactive spreading occurs, the forces at the three-phase line are not balanced and the line of contact between the three phases moves toward a metastable or equilibrium value. We showed previously that a line of hydrophobic SAM only 100 nm wide in an otherwise hydrophilic surface of carboxylic acid-terminated SAM stopped the spread of water and pinned the liquid.[22] Thus, for autophobic pinning to occur, a small region—less than 100 nm wide, but larger than the dimensions explored by thermal fluctuations and vibrations—must support a sufficiently organized SAM to allow the liquid to dewet and to nucleate retraction of the liquid.[22]

In an autophobic system, reactive autophobic spreading and autophobic pinning of liquid thiols on gold reflect differences in rates of formation of organized SAMs: pinning requires rapid formation of an organized, autophobic SAM. Differences in rates may arise from differences in the rate of reaction of the liquid with the surface or of mass transport of reactants to the three-phase contact line. Other processes—for example, fluctuations in the position of the drop edge due to thermal or vibrational effects, or the details of movement of the liquid across a rough surface—may also influence the probability of spontaneous dewetting of a surface as the SAM forms

and, thus, the transition from reactive spreading to autophobic pinning.

System Chosen for Study

We have studied the reaction of hexadecanethiol. HS-$(CH_2)_{15}CH_3$ (HDT), with polycrystalline gold substrates to establish conditions that lead to autophobic pinning of this liquid on gold. Freshly evaporated gold has a high surface tension (γ_{sv} > 500 erg/cm²) and is wet readily by almost all organic liquids;[23] useful exceptions are liquid alkanethiols (see below). The gold studied in this work has been exposed to the atmosphere of the laboratory and is covered with a thin, disorganized surface layer of adsorbed impurities. HDT forms excellent SAMs on gold; the surface of a fully formed SAM of this thiol has a low interfacial free energy: $\gamma_{sv} \sim 20$ erg/cm² ($\theta_a(H_2O) \sim 112-115°$).[24-28]

HDT is a liquid at room temperature with a surface tension, γ_{lv}, of ~32 erg/cm². HDT freezes at 18 C and boils at 250 °C. The vapor pressure of HDT at room temperature is low, and little transport of HDT through the vapor phase occurs at atmospheric pressure:[29] no derivatization of bare gold that was evident by scanning electron microscopy or wettability occurred when a 1-μL drop of HDT was held within ~10 μm of a bare gold surface for 1 min. Applications of autophobic pinning to the formation of SAMs patterned in small features require minimum transport of thiol through the vapor phase to achieve high resolution in boundaries between regions of different SAMs. Thiols more volatile than HDT—for example, undecanethiol—that otherwise meet the criteria for autophobic pinning of their liquids yield patterns with low edge resolution at room temperature because SAMs form outside of the region of contact of liquid and solid gold.

Experimental Section

Materials. Dioxygen was removed from absolute ethanol (Quantum Chemical Corp.) by bubbling N_2 or Ar through it before use. Hexadecane (Aldrich, 99%) was percolated twice through activated, neutral alumina (EM Science). Water was deionized and distilled in a glass and Teflon apparatus. Thiols and disulfides were available from previous studies.[31-33] Gold substrates were prepared by e-beam evaporation (using a deposition rate of 1 A/s) of either 1000 or 75 Å of gold (99.999%) onto Ti primed (5 Å) silicon wafers (Silicon Sense) at a pressure of 1×10^{-7} Torr.[33]

Methods. In most experiments, a Micro-Electrapette syringe (Matrix Technologies) equipped with disposable polystyrene pipette tips was used for dispensing and removing liquids from the SAMs (~1 μL/s). In a few experiments, the reservoir for hexadecanethiol (HDT) was a Staedler pen (Model 757-060) equipped with a tungsten tip. The reservoir of liquid in either case was fixed above a precision stage (Newport Optics) that

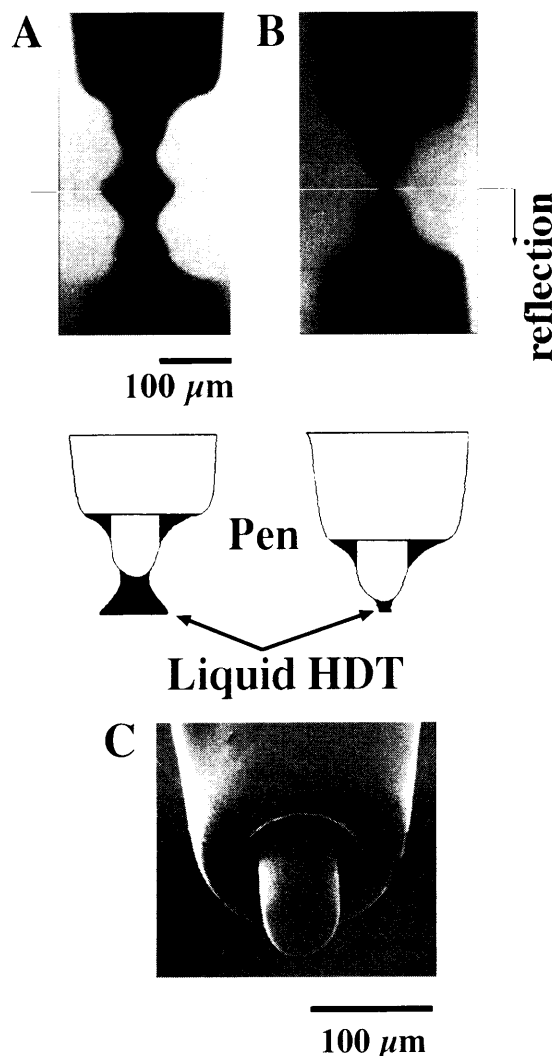(17) Kloubek, J. *J. Colloid Interface Sci* **1974**, *46*, 185–190.

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Figure 2. A drop of neat hexadecane in contact with the surface of bare gold was pinned by reaction with the surface. (A) The advancing contact angle of neat HDT on gold (~1000 Å of Au supported on a silicon wafer) was 54°. The picture shows the drop and its reflection on gold. (B) The area of contact between a 3-nL drop of HDT and gold was ~100 μm². The column of liquid remained stable and confined as the gold substrate was moved at a rate of ~100 μm/s. (C) SEM image of the tip of the pen used to hold HDT.

held the gold substrate; the substrate was translated underneath the tip of the reservoir of liquid. The tip did not touch the surface of the gold. Figure 2 shows a magnified view of drops of HDT in contact with bare gold. We chose the angle of observation to be ~2° above the plane of the sample; this angle provided a view that contained both the drop and its image mirrored in the gold surface. The presence of image and mirror image defined the drop edge clearly and allowed accurate determination of contact angles.

Stamps were made of poly(dimethylsiloxane) (Dow-Corning, SYLGARD Silicone Elastomer-184).[6,7] The stamps were inked with neat hexadecanethiol and placed in contact with the surface of the gold substrate for 5 s. The sample was rinsed with ethanol (~20 mL) and dried under a stream of nitrogen.

Optical micrographs were obtained by using a home-built, horizontal microscope. The objective lens (Olympus 10×; numerical aperture of ~0.15) was attached to a charged-coupled camera (NEC Model NX18A) through a relay telescope and condensing lens (10×) and digitized with a frame grabber (RasterOps, Santa Clara, CA). This system could magnify the profile of the drop up to 550 times. Movement of drops observed through the telescope was recorded at 33 frames/s using a four-head video recorder (Mitsubishi Model 52A). The source of illumination was placed behind the sample. Contact angles of liquids on gold substrates were measured directly from digitized

images of the profile of drops of these liquids on the gold substrate using IMAGE 1.53 software (National Institutes of Health).

Instrumentation. Atomic force microscopy (AFM) used a Topometrix TMX 2010 scanning probe microscope. The images were obtained using a cantilever made from silicon nitride in constant contact with the surface. The cantilever tip was scanned across the substrate at a rate of 10 μm/s and with a constant force of ~0.1 nN; data were collected in the forward part of the scan. All images were acquired in air. Images by lateral force microscopy (LFM) were obtained simultaneously with images by AFM.

Ellipsometric measurements were performed on a Rudolf Research Type 43603-200E ellipsometer equipped with a He–Ne laser (λ = 6328 Å) at an incident angle of 70°. Samples were rinsed with ethanol and dried in a stream of nitrogen prior to characterization. Values of thickness were calculated using a program written by Wasserman,[34] based on an algorithm by McCrackin and co-workers;[35] the calculation assumes a refractive index of 1.45 for the SAMs.

X-ray photoelectron spectra (XPS) were obtained on an SSX-100 spectrometer (Surface Science Instruments) using monochromatic Al Kα X-rays. A 1-mm² spot and an analyzer pass energy of 50 eV were used for measurements of C(1s) and Au(4f); these spectra were acquired for 20 and 3 min, respectively.

Results and Discussion

Drops of HDT are autophobic, and do not spread, on gold (Figure 2). A drop of HDT placed in contact with the surface of 1000 Å thick gold films had an advancing contact angle (θ_a) of 54° and a receding contact angle (θ_r) of 47°. The contact angles of HDT on bare gold were indistinguishable from contact angles of HDT on SAMs formed from ethanolic solutions of HDT. This observation indicated that complete SAMs form when a drop of HDT contacts bare gold.

Lateral force microscopy (LFM) showed that the boundary between areas derivatized by HDT (by application of a drop of this liquid or using μCP) and bare gold was sharp (<0.5 μm wide) (Figure 3). Bis(carboxyhexadecyl) disulfide rather than the analogous thiol was used to fill in the bare regions of the surface because the disulfide reacts with bare regions of the gold ~10³ times faster than regions protected by HDT.[36] The contrast in LFM between adjacent regions with these different SAMs reflects (we presume) differences in their friction with the tip. We have not defined the origin of these differences in any detail.

The texture evident in the LFM images paralleled the surface topology measured simultaneously by AFM; this surface topology is due to crystallites of gold formed during deposition of the gold. The greater differential force measured by LFM in regions between crystallites, where curvature of the gold surface is greater than on top of crystallites, may reflect higher capillary effects on the AFM tip due to the adsorbate film and the roughness of the gold (Figure 3d). The differential force measured by LFM was relatively higher between crystallites in carboxylic acid-terminated regions than between crystallites in CH₃-terminated regions, probably because of the greater surface tension of the former.

The sharp boundary between different SAMs in the high magnification image in Figure 3 followed borders between crystallites. We found previously that morphology of gold surfaces significantly affected the hysteresis in the forward and receding contact angles of liquids of SAMs formed on polycrystalline gold with different thicknesses.[33] We

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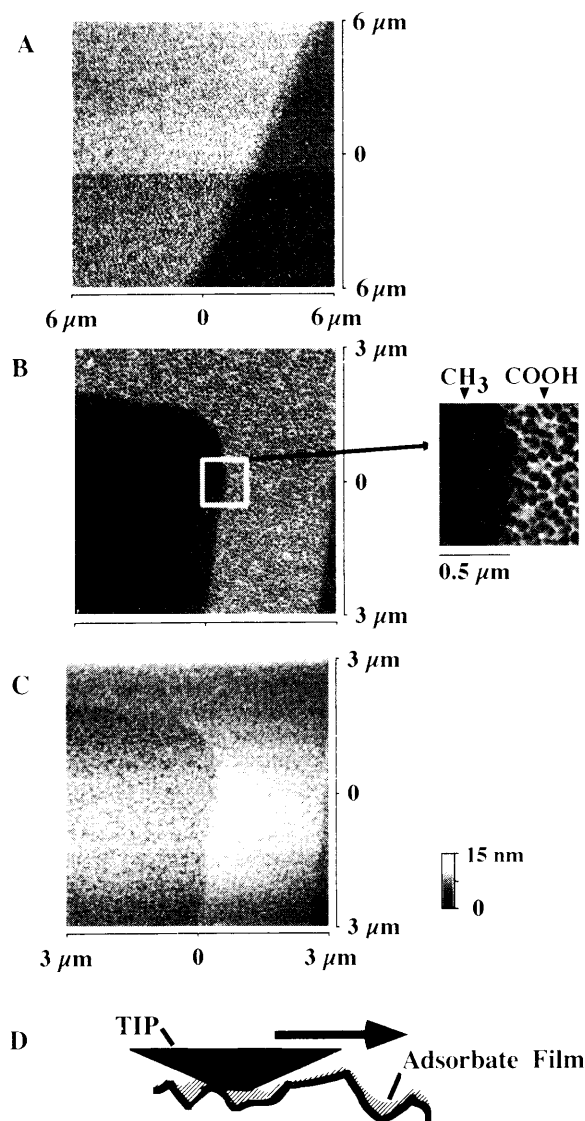
Figure 3. (A, B) Lateral force microscope image of the boundary between regions of gold derivatized by HDT, applied either as a drop of its neat liquid (a) or using a PDMS stamp inked with HDT (b), and adjacent regions derivatized by immersion of the sample in a solution of bis(carboxyhexadecyl) disulfide to complete the SAM. This boundary was sharp ($<0.5\mu m$). Areas on the gold derivatized by HDT (CH_3) appear dark (low differential force on the cantilever tip) and areas of gold terminated in carboxylic acids (COOH) appear light (high differential force on the cantilever tip). The area bordered in white in this image is enlarged to the right. The change in brightness evident in (a) as a horizontal boundary in the middle of this image probably resulted from a dust particle picked up on the tip as it scanned the surface. These images represent the raw data from the photodiode used to monitor the force on the tip and were not filtered or otherwise processed. (C) The topology of the sample measured by atomic force microscopy. The mean deviation of the peaks and troughs of the crystallites from the average plane of the sample was ~8 nm. Regions of the surface terminated with SAMs formed from bis(carboxyhexadecyl) disulfide appeared higher by ~2 ± 1 nm than adjacent regions formed from HDT, perhaps because the carboxylic acid-terminated regions were covered with an adsorbate film. (D) Schematic representation of AFM tip in contact with the gold surface.

suggest that the sharp boundary between adjacent SAMs in Figure 3 is direct evidence that surface morphology influences the spread of liquid HDT on gold. An estimate from Figure 3c suggests that "valleys" approximately ~20 nm across between "hillsides" of gold crystallites approximately 100 nm across were able to block the spread of liquid.

Influence of Surface Contaminants on Spreading. We wanted to examine the effect of adsorbates on bare gold on the spread of drops; μCP is usually done in the environment of the open laboratory where some degree of contamination of the gold is a certainty. Dihexyl sulfide (($CH_3(CH_2)_5)_2S$) forms SAMs on gold in which the R_2S groups are weakly bound to the gold surface; these physisorbed dialkyl sulfides are displaced readily by thiols.[31,37] Drops of HDT placed on gold derivatized with dihexyl sulfide initially spread and formed an extended film of liquid on its surface; after approximately 30 s the film of HDT spontaneously retracted on the surface and formed a drop. This behavior reflects initial wetting of the SAM of dihexyl sulfide by liquid HDT, followed by displacement of the dihexyl sulfide from the surface by HDT and formation of a SAM of hexadecanethiolate not wet by liquid HDT. If the initial SAM was formed from a species—ethanethiolate—that was more strongly adsorbed on gold than dihexyl sulfide, a considerably longer time (25 min) was required before the liquid film of HDT spontaneously retracted into a drop.

The practical implication of these observations for μCP rests on the requirement that an autophobic SAM be formed rapidly (~1 s, see below) to achieve sharp features. To accomplish this objective, the surface of gold must be free of strongly coordinated (and slowly displaced) adsorbates.

Influence of the Concentration of HDT on the Autophobicity and Spreading of Its Drops. A decrease in concentration of alkanethiols in ethanolic solutions slows the rate of formation of SAMs on gold from these solutions.[31] We used drops of HDT diluted with hexadecane, a liquid with a volatility, surface tension, and viscosity similar to that of HDT (but unable to form SAMs on gold) to study the effect of the concentration of HDT on the spread of its solution.

Drops of hexadecane with different concentrations of HDT, suspended at the tip of a pipette (Figure 2), made contact with bare gold, advanced, and stopped. Continuous translation of the gold substrate caused, in order, three events: (i) the drop edge remained stationary and its contact angle increased continuously to a maximum characteristic of the concentration of thiol and rate of translation of the substrate; (ii) the drop edge "spilled" forward; (iii) the advance of the drop edge stopped after some distance. This sequence repeated. The drop thus appeared to "jump" across the bare gold surface as the substrate translated smoothly beneath the drop. The discontinuous movement of drops of HDT on bare gold contrasts with their movement on gold with preformed SAMs: in the latter system, the drop edge moved to its maximum advancing contact angle and this angle remained constant as the drop edge moved continuously across the surface at the rate of translation of the substrate.

Examination of liquid HDT in this system provided limits to the influence of concentration on the spread of its drop on gold. Translation of the gold substrate underneath the pipette first caused the leading edge of the drop to advance to a maximum contact angle of ~53°. This angle is the same as the maximum advancing contact angle of liquid HDT covered by a SAM of hexadecanethiolate. Continued movement of the substrate made the drop "jump" forward. We imagine that the edge of the drop crossed the boundary (similar to those shown in Figure 3) between SAM and bare gold at this point. Because γ_{sv} no longer equaled $[\gamma_{sl} + \gamma_{lv} \cos \theta]$ (eq 1), the drop edge, unbalanced by surface tension, began to spread.

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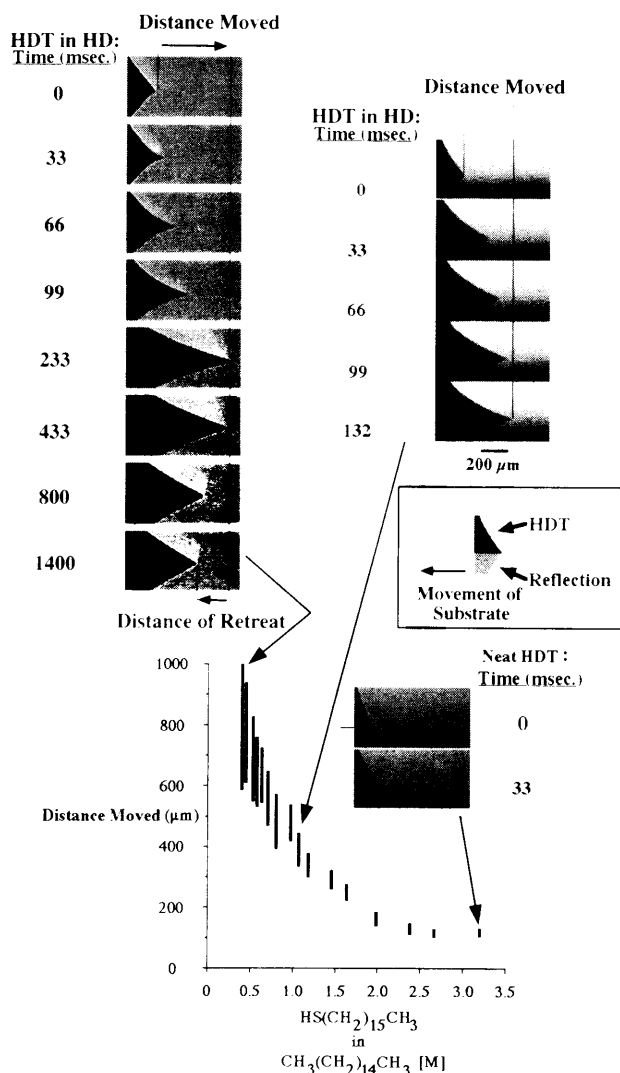
Figure 4. Distance jumped by drops of solutions of HDT in hexadecane decreased with increased concentration of HDT. In these experiments, the drop was held stationary and the substrate was translated beneath it. Stacked images show successive frames of the drops and thus record its movement until forward progress of the macroscopic liquid front stopped. For the set on the left, the spontaneous retreat of the drop edge is also shown. "Neat" HDT is the liquid undiluted by hexadecane. The spread in the data reflects results from at least 10 measurements at each concentration. The volume of these drops was ~1 μL.

This spreading, aided by gravity and surface tension, caused the leading edge of the drop to advance rapidly. Movement of the drop stopped when the advancing contact angle of the liquid in the region of the gold surface near the advancing edge of the drop became finite because of reaction between the liquid HDT and the surface, and formation of an organized SAM of HDT not wet by liquid HDT occurred.

The distance "jumped" by the drop depended on the concentration of HDT. We measured the distance moved by the drop after it jumped forward until it stopped: this measure supported the hypothesis that pinning of drops depended on the kinetics of reaction between the drop and bare gold. Drops with high concentrations of HDT in hexadecane moved a shorter distance than did drops with low concentrations of HDT (Figure 4). When the contact angle of the advancing front of liquid fell below the receding angle of HDT on a fully formed monolayer of hexadecanethiolate (< ~46°, demonstrated by the last picture in each sequence of frames in Figure 4) the drop edged reversed its direction of movement until the contact

angle was the equal to the receding angle on the surface (sequence of frames on the left of Figure 4). Retraction of the drop edge occurred when it dewet the surface and was not an artifact of the forward translation of the substrate, which was slow compared to movement of the drop edge in either direction. We were able to observe the reversal in direction of movement of the drop only for concentrations of HDT below ~0.5 M, although it probably occurred for all the solutions we tested. The speed of the reaction at [HDT] > 0.5 M, and the rapid movement of the drop edge relative to the speed at which we could capture images, prevented observation of contact angles lower than the equilibrium receding contact angles for these solutions. The increased range in the distance jumped by the drop edge (indicated by the height of the bars in the graph in Figure 4) as the concentration of HDT in drops decreased seemed to result from the sensitivity of the kinetics of pinning to heterogeneities on the gold surface (perhaps adsorbed impurities or small differences in morphology).

These observations imply that mass transport of thiol to the surface of gold, and not the rate of the reaction of thiol with gold, limits the pinning of liquids with [HDT] < 1 M on gold at room temperature.[36] In contrast, the rate of formation of SAMs at [HDT] > 1 M is rapid, as judged by the short distance of travel of neat HDT (Figure 4). For these high concentrations of thiol, the coverage of gold is probably close to unity during the time of advance of the solution. The observation that the advance of the drops still occurs in steps suggests that displacement of impurities and perhaps the reaction and organization of the SAM also contribute to the rate at which HDT can spread. The role of adsorbates on the gold surface and the roughness of the gold surface ultimately limit the reaction of thiols with this surface and constrain pinning of these liquids, and the ultimate resolution of patterning, on gold surfaces.

Reactive Autophobic Spreading. Dilute (<0.1 M) solutions of HDT in hexadecane were autophobic, but not pinned, on bare gold. We did not ascertain the minimum concentration of HDT necessary to pin drops of its solution with hexadecane, although we estimate from the data in Figure 4 that this concentration was >0.1 M. Below this concentration, a drop of HDT in hexadecane spread reactively. The advancing edge of a drop of HDT was no longer pinned, because formation of a low energy monolayer was limited by mass transport of thiol to gold and was thus too slow to stop the spread of the drop. The trailing edge, by contrast, dewet from a more organized SAM and had a higher contact angle.

We observed that drops of 1 mM solutions of HDT spread reactively across the surface of gold: the drop was pushed forward, at rates up to ~1 mm/s, by its finite receding contact angle on the surface (Figure 5). The drop spread symmetrically as it made contact with the surface; its shape was a spherical cap; its forward progress slowed as the drop flattened and the pressure to spread decreased (Figure 5a).[38,39] Reaction with the surface and organization of the resulting SAM caused one part of the advancing edge of the drop to peel back and pushed liquid to regions of the drop where the contact angle was <5° (Figure 5b). The drop began to move in the direction where its contact angle remained low. Its shape was asymmetric: a lead edge where the contact angle with the surface was <5°, and a back edge where the contact angle with the surface was ~40° (Figure 5c). The drop gained speed until it reached a constant value. Solutions of HDT moved

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Rate of Travel ~ 1 mm /sec.
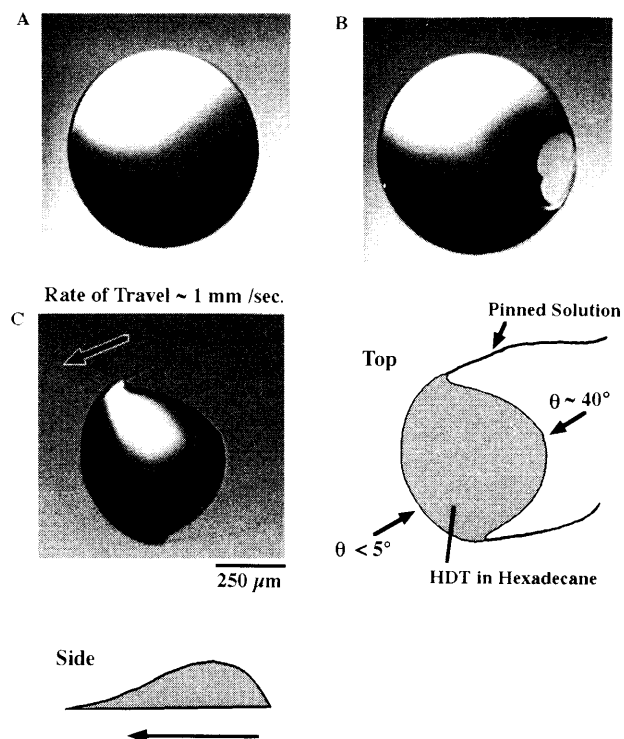
Figure 5. Drops of 1 mM HDT in hexadecane moved, and were not pinned, across the surface of bare gold at rates of ~1 mm/s. The volume of these drops was ~5 μL. (A) The drop shape after 1.267 s of contact with the bare gold surface. (B) The drop 0.067 s later than A, begins to dewet the gold because SAM formation results in a finite contact angle between the drop and the surface. (C) The drop 2.000 s later than B, pushed forward at a steady rate of 1 mm/s.

across the bare gold surface until reaction with gold depleted its thiol or the surface of the gold was covered by SAMs. Drops spreading reactively deflected off regions on the gold already derivatized by SAMs. Higher concentrations (> 1 mM) of HDT caused its liquid to peel back in two or more areas after contacting bare gold before a preferred direction of displacement of liquid was selected and movement as a drop occurred. At still higher concentrations of HDT (~100 mM) the drop pinned: retraction of its solution occurred simultaneously at many points on the perimeter of the drop so that no preferred direction of displacement of liquid occurred.

Liquid trails left behind by the passage of the drop on the surface seemed to result from pinning of these solutions. More dilute solutions of HDT ([HDT] < 1 μM) drops did not spread reactively, although the liquids remained autophobic: the liquid spread across the entire sample uniformly; several minutes passed before this film of liquid became unstable and broke up into small drops with finite contact angles.

Autophobic Pinning of Drops of Mercaptohexadecanol in Hexadecane. The qualitative study of drops of HDT on gold described in the preceding sections provided enough information about autophobic pinning of drops to suggest ways to extend the scope of this phenomenon. In particular we wished to be able to form patterns from thiols having terminal groups other than CH_3. Forming patterned SAMs in air requires thiols that yield SAMs with low values of γ_{sv}: these SAMs make the system hydrophobic. We hypothesized that a second liquid phase, immiscible with the drop, could be used instead of air to pin these drops in contact with gold. In particular we predicted that drops of 16-hydroxyhexadecanethiol (HHT) in solutions of hexadecane would pin on gold when these drops contacted gold *under water*. HHT forms SAMs
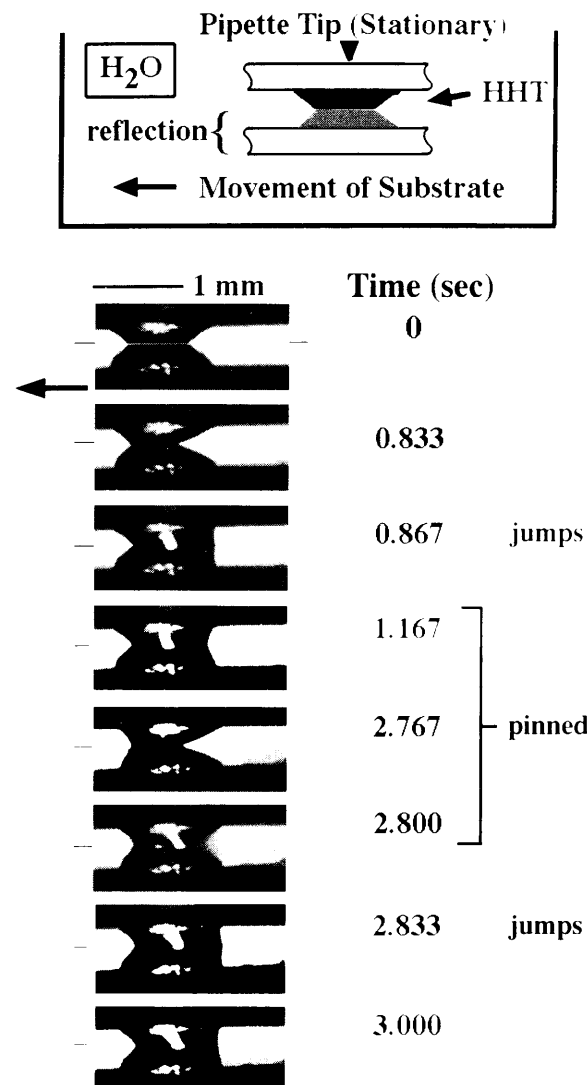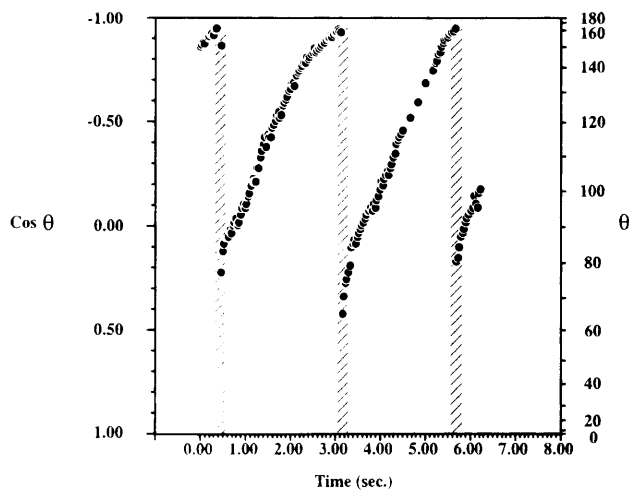

Figure 6. Drops of 5 mM HHT in hexadecane were pinned, under water, on bare gold. Each picture was taken from a sequence recording the contact angle of these drops (and their reflection) as the gold substrate they contacted moved at a rate of 0.1 mm/s.

that are ordered and hydrophilic: the advancing contact of water in air on these SAMs is ~10−20°. We expected water to wet preferentially the hydrophilic SAMs that resulted from reaction of drops of HHT with bare gold; the interfacial tensions between the solution, water, and the hydrophilic SAMs would pin the drop.

Drops of 30 mM HHT in hexadecane spread reactively over bare gold in air and are not autophobic; the advancing contact angle of this solution on a SAM of HHT, in air, was <5°. HHT in hexadecane was pinned, however, when drops of this solution contacted bare gold through water (Figure 6). The contact angle of 5 mM solutions of HHT in HD were θ_a = 165° and θ_r = 135° on SAMs of HHT under water. By contrast, under water neat HDT spread on bare gold (θ_a < 5°). Under water, the hydrophobic SAM formed by reaction of HDT with the gold surface was preferentially wet by hexadecane.[40] When the gold substrate moved below drops of HHT in hexadecane in contact with the gold under water, these drops remained confined and pinned; movement occurred only when the edge of the drop exceeded its maximum advancing contact angle, under water, on SAMs formed from HHT (Figure 7). The movement of drops of HHT on bare gold under

(40) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 2790–2793.

Figure 7. Advancing contact angle, under water, of drops of 5 mM solutions of HHT in hexadecane on bare gold undergoes sharp, and reproducible, transitions due to pinning its leading edge by reaction with the surface. A drop of HDT was placed in contact with gold under water, and the gold was moved at a rate of 0.1 mm/s; when the advancing contact angle reached ~165°, the drop edge jumped forward spontaneously at a rate of ~15 mm/s until it was again pinned. The striped regions indicate that forward movement of the drop, and its contact angle, was faster than could be resolved by our video equipment: Lower advancing contact angles during these transitions in contact angle may exist, but we cannot measure them. These data represent the whole record of the sequence of contact angles of drops of HHT in hexadecane summarized in Figure 6.

water was like that of drops of HDT in air; the drop jumped periodically in response to the continuous translation of the gold substrate.

One feature of the data evident from Figure 6 was the high speed of jumping and the short distance traveled by drops of solutions of HHT under water (compared to drops of HDT in air). Since the kinetics of formation SAMs of HHT or HDT were probably similar at the same concentration of thiol, differences in the movement of drops in

air or under water might reflect differences in the spreading pressure[39] and/or damping effects due to displacement of water or impurities. The high contact angle of solutions of HHT under water ($\theta_a = 165°$) resulted in a large difference in pressure when the drop edge crossed the boundary between the SAM and bare gold and caused the initial rapid movement of the edge of the drop. Displacement of water, or impurities on the gold surface, damped this forward movement (compared to the case in air). The solution of HHT thus moved forward quickly but traveled only a short distance.

These observations demonstrate that patterning gold by contact with solutions of thiols under water is practical. This technique should extend the utility of autophobic pinning in the placement and control of these drops.[8] The thiol can be solid or volatile because immiscible liquids are used to confine the phases. A wide range of terminal functional groups result in pinning when solutions of these thiols are brought into contact with bare gold under water; drops of 5 mM solutions of hydroxy-, carboxy-, and nitrile-terminated thiols in hexadecane all pin under water.

Conclusions

This paper establishes conditions necessary for autophobic pinning of solutions of alkanethiols by their reaction with a surface. Interfacial tension and the kinetics of organization of the SAMs are important considerations in the design of systems to limit the spread of drops. The two systems investigated in this paper—one producing low-energy surfaces under air and the second producing hydrophilic surfaces under water—provide a basis for understanding one aspect of the mechanism of μCP based on the reaction of thiols with bare gold and a rationale for its extension to patterned SAMs terminated in hydrophilic SAMs.