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Directed Movement of Liquids on Patterned Surfaces Using Noncovalent Molecular Adsorption

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Pressure gradients provided by pumps or external forces govern the flow characteristics of fluids within many pipes and other conduits.[1] For microfluidic systems, the description of liquid flows becomes complicated due to the presence of capillary forces that can affect the controlled delivery of liquids within microelectromechanical systems (MEMS) or to different chambers within a microreactor network.[2] As an alternative to macroscale methods for delivering liquids within microscale systems, the transport of liquids can be driven on surfaces by a gradient in wettability.[3−5] These gradients can be generated passively using surfaces with spatial variations in free energy or actively using adsorbates that decrease the wettability of the surface and induce a localized dewetting by the liquid (Figure 1). This latter topic has been the subject of recent theoretical studies;[6−8] however, complementary experiments are lacking due to difficulties in controlling the direction of drop movement and modulating the responsible surface interactions. Previous examples of adsorption-driven drop movement include those based on the irreversible attachment of adsorbates to a substrate.[3,9] Such systems are single-use and can only transport one drop on their surface as the reacted surface does not allow further adsorption by a subsequent adsorbate. In contrast, surfaces with fixed spatial gradients in wettability offer an alternative for directing liquid movement.[3] These systems are reusable but are limited by hysteresis effects to the delivery of liquids over short distances.[10] The procedure detailed here overcomes these various limitations and provides a new direction for both fundamental and practical studies of surface-mediated drop movement. Specifically, the detailed system allows the relationships between surface energetics and drop movement to be revealed experimentally for the first time.

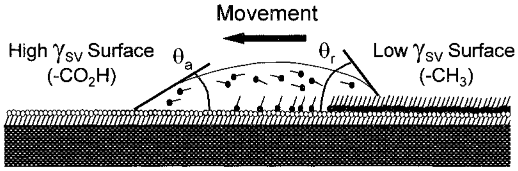

Figure 1. Schematic cross-sectional view of a moving drop. In the present work, the lowered surface energy (γ_{LV}) is generated by the adsorption of an *n*-alkylamine within the drop onto a high-energy CO_2H surface to produce a lower energy CH_3 surface.

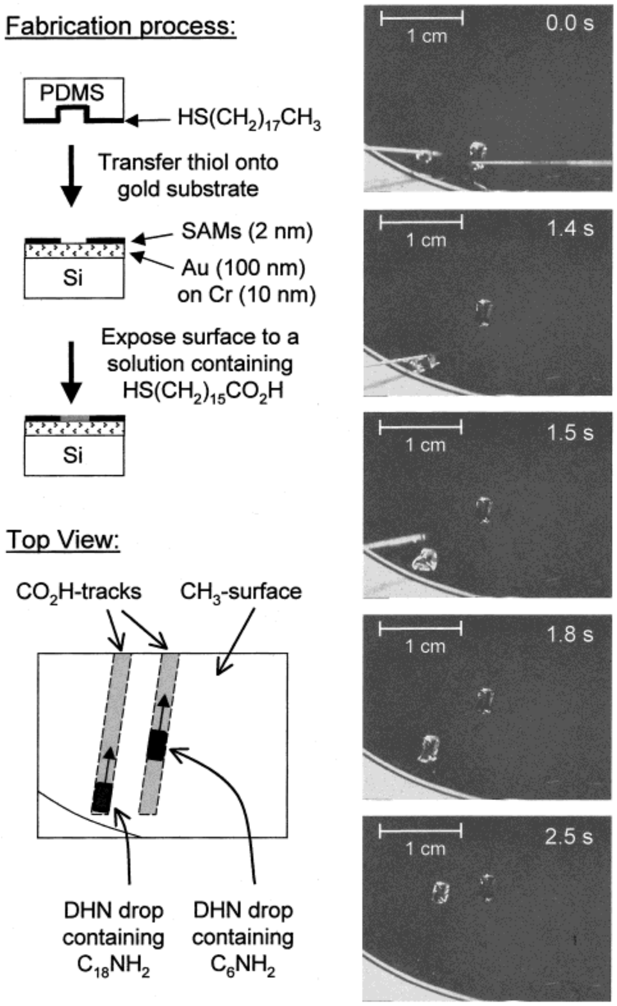

Figure 2. Schematic illustration of the fabrication process and images showing the movement of two alkylamine-containing DHN drops on a patterned gold surface. Upper left: The surface patterning employed microcontact printing to produce 2 mm wide CO_2H-exposing tracks surrounded by a CH_3 surface. Right column: Drops containing 1 mM C_6NH_2 (right) and 1 mM $C_{18}NH_2$ (left) were applied on different tracks (2 mm wide × 60 mm long) expressing CO_2H groups. The surrounding CH_3-terminated domains restrict the movement of the drops along specific paths (lower left). The $C_{18}NH_2$-containing drop was deposited on one end of the left track ∼1.5 s after the C_6NH_2-containing drop began to move. The $C_{18}NH_2$ drop reached the same position as the slower C_6NH_2-containing drop within ∼1 s and later passed it.

To direct the liquid movement, we employed microcontact printing to pattern solid substrates with two different self-assembled monolayers (Figure 2).[11] The stamp was fabricated by casting poly(dimethylsiloxane) (PDMS) on a photolithographically prepared master that contained two parallel 2 × 60 mm^2 rectangles as features. The PDMS stamp was "inked" with a 5 mM ethanolic solution of octadecanethiol ($CH_3(CH_2)_{17}SH$) and transferred the thiol to specified areas of a gold surface. The remaining surface was derivatized by immersion in a 5 mM ethanolic solution of 16-mercaptohexadecanoic acid ($HS(CH_2)_{15}CO_2H$) to complete formation of 2 × 60 mm^2 CO_2H-terminated tracks surrounded by a low-energy CH_3-terminated surface. When a 1 μL drop of decahydronaphthalene (DHN)[12] containing 1 mM alkylamine ($CH_3(CH_2)_{n-1}NH_2$ or C_nNH_2) was applied to a track terminus at

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(10) These systems require a continuous change in surface energy, and its gradient must be greater than the resistance to drop movement provided by the difference in the advancing and receding wetting properties of the liquid.

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the boundary of the CO_2H and CH_3 regions, the drop spontaneously moved along the length of the CO_2H track as a discrete object (Figure 2) and left behind an oriented monolayer of the alkylamine that exposed a CH_3 surface. Complementary experiments using reflectance infrared spectroscopy indicated that the adsorption of the amine layer on the CO_2H surface results from acid−base interactions and forms a densely packed molecular film that exposes CH_3 groups at its surface.[12] The adsorption process responsible for drop movement worked best with nonpolar liquids, and the dewetting of the newly formed CH_3 surfaces to allow drop movement required that the surface tension of the liquid be greater than ∼30 mN/m.[13]

DHN drops containing longer chained alkylamines moved at faster velocities than those containing shorter chained alkylamines (Figure 2). The resulting noncovalently adsorbed amine layers could be removed by rinsing the substrate with polar solvents such as ethanol or water to regenerate the original patterned CO_2H/CH_3 surfaces for the delivery of additional drops. The noncovalent nature of the interaction between the adsorbed alkylamines and the CO_2H surface allowed replacement of a deposited amine adlayer by exposure to a solution of a second longer chained alkylamine. For example, when a bilayer assembly derived from C_6NH_2 was immersed in a 1 mM DHN solution of $C_{18}NH_2$, the ellipsometric thickness, wetting properties, and infrared spectrum of the resulting film were the same as for the direct assembly of $C_{18}NH_2$ onto a CO_2H surface. The replacement of the adsorbed amines occurred within seconds of contact with the $C_{18}NH_2$ solution and produced a lower energy, more oleophobic surface. The concurrent changes in surface energy provided the conceptual basis for delivering two drops sequentially on a common surface. For example, on the patterned substrate, the placement of a drop of 1 mM C_6NH_2 in DHN at one end of a track resulted in its movement over the track and the deposition of a C_6NH_2 layer as in Figure 2. Placement of a $C_{18}NH_2$ drop at the same end of this C_6NH_2-derivatized track resulted in the movement of this second drop along the same path as the C_6NH_2 drop and the deposition of an oriented film of $C_{18}NH_2$ in place of the C_6NH_2 adlayer. The ability to replace the C_6NH_2 layer and further reduce the surface energy of the track by the adsorption of $C_{18}NH_2$ provided the energetic requirements for this sequential delivery of drops to proceed on the surface. The $C_{18}NH_2$ drop in this two-drop experiment moved with roughly half the velocity of a $C_{18}NH_2$ drop deposited on a bare CO_2H surface.

In these various experiments, the dominant force responsible for drop movement is the unbalanced Young force, F_Y,[3,14] that results from the difference in wettability or surface energy between the front and backsides of the drop (Figure 1):

$$F_Y = \gamma_{LV}(\cos\theta_a - \cos\theta_r) \tag{1}$$

where γ_{LV} is the surface tension of the liquid, and θ_a and θ_r are the advancing and receding contact angles for the drop, respectively.[15] As DHN wets CO_2H surfaces, $\theta_a \cong 0°$; therefore, the exerted F_Y directly depends on θ_r when a monomolecular film of the alkylamine is deposited on a bare CO_2H surface. With increasing chain lengths of the alkylamine, θ_r increases in value and effects a greater F_Y on the drop as manifested by an increase in drop velocity with increasing chain length (Figures 2 and 3). For the $C_{18}NH_2$ drop on the C_6NH_2-derivatized track, the original surface is less wettable and $\theta_a \cong 32°$. As a result, F_Y is reduced relative to a bare CO_2H surface and the $C_{18}NH_2$-containing drop moves with a lower velocity than when deposited on the CO_2H surface.

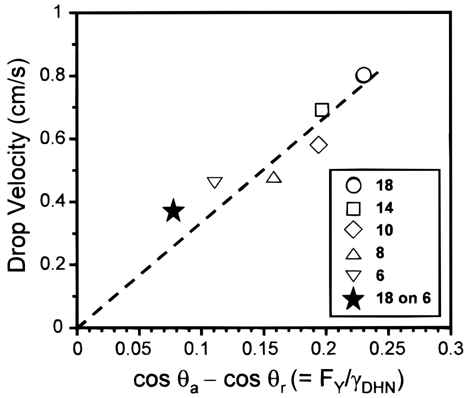

Figure 3. The velocity of DHN drops containing various alkylamines (C_nNH_2) on bare CO_2H surfaces (open symbols) and an adsorbed film derived from C_6NH_2 on a CO_2H surface (filled symbol) with respect to ($\cos\theta_a - \cos\theta_r$). The dashed line is a linear fit to the data.

Figure 3 plots the steady-state velocities for alkylamine-containing drops of DHN on the CO_2H surface with respect to their values of the quantity, $\cos\theta_a - \cos\theta_r$ (i.e., F_Y/γ_{LV}). As indicated by the line in Figure 3, the velocity appears to be proportional to the difference between $\cos\theta_a$ and $\cos\theta_r$. This observation can be explained by equating the unbalanced Young force of the surface with the drag force on the moving drop:

$$W\gamma_{LV}(\cos\theta_a - \cos\theta_r) = A\mu\frac{v}{h} \tag{2}$$

where μ is the viscosity of the liquid, v is the drop velocity, W is the length of the contact lines at the front and rear of the drop and is roughly the width of track, A is the contact area between the drop and the substrate, and h is a characteristic length that approximates the mean height of the drop as averaged over the drop/substrate contact area with respect to the local drag force. The proportionality constant, $(Wh\gamma_{LV})/(A\mu)$, obtained from Figure 3 is approximately 3 cm/s, with the value of h being roughly a micrometer suggesting that the drag force is localized primarily near the contact lines.[16]

The present work demonstrates that liquid drops can be delivered laterally along specified paths using patterned surfaces and a driving force for motion based on molecular adsorption. The velocity of the drops on these surfaces can be manipulated by selection of the molecular structure of the incorporated adsorbate. A particular feature of the detailed adsorption chemistry is its reliance on a noncovalent adlayer that can allow the sequential transport of two drops along a common specified path and the ability to regenerate the active surface for further use. The strategies used here should be amenable for designing three-dimensional systems, where adsorption processes onto the functionalized walls of a channel would cause spontaneous liquid movement. Such systems would offer a new strategy for the design of microdevices that must deliver small volumes of chemical reagents or analytes within their channeled networks. Further work to examine the effects of adsorbate concentration, drop size, and track geometry is presently underway and illustrates the richness of this new experimental platform for studies of chemically directed drop movement.

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(12) We note that noncovalent interactions between functional groups such as $CONH_2$−$CONH_2$ and CO_2H−$CONH_2$ also produce drop movement.

(13) A condition for drop movement is that the advancing contact angle on one side of the drop be less than the receding contact angle on the other side of the drop (Figure 1). On the CH_3 surfaces produced by the adsorption of the alkylamines, a minimum surface tension of ∼30 mN/m was required to achieve a nonzero receding contact angle and allow drop movment.

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