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# Modeling Organic Surfaces with Self-Assembled Monolayers \*\*

**Interfacial Structure  
Wettability  
Long-Chain Thiols  
on Gold**

By Colin D. Bain\* and George M. Whitesides\*

The interfacial properties of organic materials are of critical importance in many applications, especially the control of wettability, adhesion, tribology, and corrosion. The relationships between the microscopic structure of an organic surface and its macroscopic physical properties are, however, only poorly understood. This short review presents a model system that has the ease of preparation and the structural definition required to provide a firm understanding of interfacial phenomena. Long-chain thiols,  $\text{HS}(\text{CH}_2)_n\text{X}$ , adsorb from solution onto gold and form densely packed, oriented monolayers. By varying the terminal functional group, X, of the thiol, organic surfaces can be created having a wide range of structures and properties. More complex systems can be constructed by co-adsorbing two or more thiols with different terminal functional groups or with different chain lengths onto a common gold substrate. By these techniques, controlled degrees of disorder can be introduced into model surfaces. We have used these systems to explore the relationships between the microscopic structure of the monolayers on a molecular and supramolecular scale and their macroscopic properties. Wettability is a macroscopic interfacial property that has proven of particular interest.

## 1. Introduction

Much of modern materials science has been devoted to the discovery, development and production of materials with desired combinations of bulk mechanical, electrical or optical properties. In an increasing number of materials systems, however, performance is determined not only by the properties of the bulk but also by the characteristics of interfaces either within the material or between the material and the outside world. Examples abound: the strength and toughness of a carbon fiber composite is strongly influenced by the bond between the fiber and the polymer matrix; cracks may

propagate rapidly along grain boundaries; the biological response to implanted materials is critically determined by the properties of their surfaces; surface states can pin the Fermi level in semiconductors; water and oil repellency are determined by the outermost few angstroms of a material; optical losses occur through reflection, scattering and non-linear processes at interfaces. As trends towards miniaturization continue, the ratio of surface to volume increases and the importance of understanding and controlling interfacial properties grows commensurately.

The goal of relating the microscopic (atomic, molecular and supramolecular) structure of a surface to its macroscopic physical, chemical or biological properties (wettability, corrosion resistance, adhesive strength, biocompatibility) is not trivial, and may prove as great a challenge as the development of new materials. Attaining this goal is made more difficult by the complexity and inaccessibility of many interfaces of practical importance. Consequently, the ability to create model surfaces in which the structure is controlled on an atomic scale plays a vital role. Epitaxial growth techniques, such as molecular beam epitaxy (MBE) and vacuum pyrolysis epitaxy (VPE), have provided a way forward in the study of semiconductors and ceramics, but such techniques cannot easily be applied to the synthesis of model organic surfaces. Recently it has become clear that organic monolayer films offer the level of structural control required for detailed studies of organic surfaces. Of all the types of monolayer film studied since *Benjamin Franklin* first poured oil onto Clapham Pond, two systems appear particularly promising: monolayers prepared by adsorption of alkanethiols on gold,<sup>[1]</sup> silver, copper or platinum, and those generated by reaction of alkyltrichlorosilanes with silicon or glass.<sup>[2]</sup> In this review we will concentrate on monolayers of alkylsulfur compounds on gold, with the emphasis on our own research. First, we will discuss the difference between these self-assembled monolayers and films produced by the Langmuir-Blodgett (LB) technique. We will then summarize the structural properties of monolayers generated by adsorption of thiols on gold. The bulk of the review is devoted to explaining, with examples, how the structure of the monolayer-air or monolayer-liquid interface can be varied in a controlled manner, and to discussing the types of information that can be derived from studies of model organic surfaces.

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## 2. Langmuir-Blodgett and Self-Assembled Monolayers

The traditional means of forming an organic monolayer film is to spread an insoluble compound on an aqueous subphase, compress the film mechanically with a barrier until the molecules are densely packed and oriented approximately normal to the surface, and then to transfer this monolayer, if desired, to a solid substrate by "dipping" (Fig. 1 top). Much elegant work has been performed using these LB monolayers,<sup>[3]</sup> and the LB technique is particularly useful when multilayers are desired. LB monolayers, however, suffer several drawbacks as model systems for studying interfacial properties. First, they are only metastable and tend to relax into more stable structural forms. Surface properties of LB films are most easily studied after the film has been transferred to a solid substrate, a procedure that may be complicated by changes in the structure of the monolayer during the transfer process. Second, they are not normally chemically bonded to the substrate and hence are not robust. LB monolayers can often be removed from a substrate simply by rinsing with either aqueous or non-aqueous solvents. Third, one is restricted to compounds that form LB films on water and that can be transferred intact to a substrate. It is, in particular, difficult to generate surfaces exposing polar functional

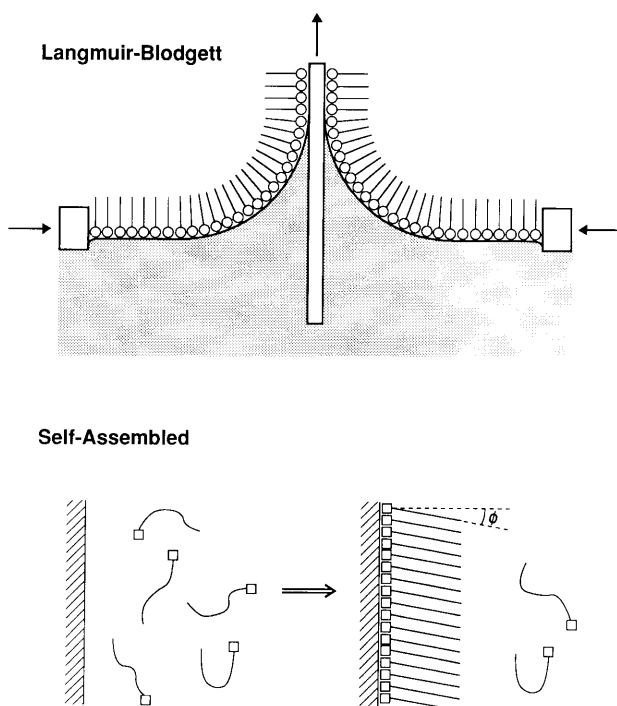


Fig. 1. Top: A Langmuir-Blodgett monolayer can be transferred from the surface of water to a hydrophilic solid by raising the substrate through the water-air interface while maintaining a constant surface pressure with movable barriers. Bottom: Self-assembled monolayers form spontaneously upon immersion of the substrate in a dilute solution of the adsorbate. Monolayer formation is driven by a strong, specific interaction between the head group (squares) and the surface of the substrate. One such system comprises thiols, RSH, adsorbed onto films of noble metals, such as gold, silver and copper. The cant ( $\phi$ ) of the hydrocarbon chains varies with the choice of substrate.

groups at the monolayer-air interface by this technique. It is also difficult to form highly crystalline monolayers since they tend to be brittle and crack easily upon compression or during transfer.

Self-assembled monolayers rely on a strong specific interaction between an adsorbate and a substrate to drive the spontaneous formation of a monolayer film (Fig. 1 bottom).<sup>[4]</sup> To prepare a self-assembled monolayer, the substrate is simply immersed in a dilute (ca. 1 mM) solution of the adsorbate at room temperature for an interval varying from a few minutes to several days, depending on the system. The principal substrate in our studies has been a gold film (1000–2000 Å thick) evaporated onto a polished silicon wafer, and we have used long-chain organosulfur compounds, typically thiols,  $\text{HS}(\text{CH}_2)_n\text{X}$ , as adsorbates. The densely packed, oriented films that result are thermodynamically stable and mechanically robust. Monolayers of thiols on gold can be removed from the solutions from which they have been adsorbed and immersed in aqueous or non-aqueous solvents, in acid or in base, without apparent adverse effects. The range of organic species that can be incorporated into these monolayers is large: few ligands compete effectively with a thiol in coordinating to the gold, and the thiol group is sufficiently unreactive to be compatible with most other functional groups. A variety of chemical reactions can also be performed on the monolayers in order to interrogate the structure or to modify the surface. Self-assembled monolayers of thiols adsorbed on gold are thus well suited for our studies.

We,<sup>[5]</sup> and others,<sup>[2, 6]</sup> have also used alkyltrichlorosilanes as precursors to monolayers of alkylsiloxanes on glass or silicon. These monolayers exhibit greater thermal, chemical (except in the presence of aqueous base) and mechanical stability than thiols adsorbed on gold: they can even be heated in boiling water or scrubbed vigorously without degradation. The high reactivity of the  $\text{SiCl}_3$  group limits the chemistry of surfaces that can be created directly by adsorption of alkyltrichlorosilanes on silicon. The thermal and chemical stability of the monolayers does, however, allow extensive synthetic modification of pre-formed films. *Ulman et al.*<sup>[6]</sup> using a modification of a technique proposed by *Sagiv et al.*<sup>[7]</sup> have recently demonstrated the feasibility of monolayer-by-monolayer synthesis of high-quality multilayer films with alkyltrichlorosilanes. These multilayers have great potential for controlling the bulk optical and electrical properties of thin films, but are beyond the scope of this review.

## 3. Structure of Monolayers of Thiols on Gold

Our investigations have centered on the adsorption onto gold of linear thiols,  $\text{HS}(\text{CH}_2)_n\text{X}$ , where  $n \geq 10$  and X is any one of a wide range of functional groups that are compatible with thiols and that do not disrupt the packing of the hydrocarbon chains. We and others have characterized the result-

ing films by a range of techniques including ellipsometry, transmission electron microscopy (TEM), contact angle determination, reflection adsorption infrared spectroscopy (RAIRS), X-ray photoelectron spectroscopy (XPS) and electrochemistry.<sup>[18-13]</sup> The picture that emerges is of a pin-hole-free, monolayer film comprising a densely packed array of *trans*-extended hydrocarbon chains, strongly anchored to the gold surface through the sulfur atom, and tilted approximately 30° from the normal to the surface. The nature of the bonding between sulfur and gold has not yet been established incontrovertibly, but available evidence points to both alkanethiols and dialkyl disulfides generating gold thiolates (Au—SR) upon adsorption. (For clarity we will use terms such as “monolayer of alkanethiol” in this review to indicate the molecular precursor, even though the actual species on the surface is probably a thiolate). The tail group, X, is the predominant chemical functionality exposed at the surface. The essential structure of the monolayer appears to be preserved for a number of tail groups exhibiting a range of intermolecular interactions.<sup>[11]</sup> Except for short chains ( $n < 10$ ), the structure of the monolayer and the properties of the monolayer–liquid or monolayer–air interface appear to be largely independent of the length of the hydrocarbon chain.<sup>[9]</sup>

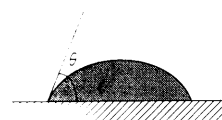
This last observation is significant. If we are to use monolayers of thiols on gold as models for other surfaces, or to study interfacial phenomena in general, it is important that the gold substrate and the sulfur–gold interface do not affect the measured properties at the monolayer–ambient interface. The gold does have an indirect effect on the properties of the monolayer through its influence on the cant of the hydrocarbon chains and hence on the orientation of the tail group at the surface of the monolayer. (If the organic monolayer is very thin, the polarizability of the gold substrate will also influence the wetting of the surface.) Small changes in the orientation of functional groups at the surface can lead to measurable changes in interfacial properties. For example, the chain tilt of monolayers of thiols adsorbed on silver is approximately zero, compared with ca. 30° on gold; the contact angle of water on a monolayer terminated by hydroxy groups on silver ( $X = OH$ ) is 20°,<sup>[16]</sup> whereas on gold angles of  $< 15^\circ$  are observed. This residual influence of the substrate is not necessarily a disadvantage: the fact that we can even ask questions about the influence of the orientation of a functional group on the macroscopic properties of an interface is a testimony to the power of the technique of self-assembly.

#### 4. Effect of the Chemical Structure of an Interface on Wettability

Wettability is a representative macroscopic physical property of surfaces that we have studied extensively. An understanding of the microscopic basis of wettability is important for two reasons: first, many technologies rely on controlling

wettability; and second, the wettability of a flat surface is determined by interfacial free energies and hence reflects intermolecular interactions at the solid–liquid and solid–vapor interfaces.<sup>[11]</sup> In fact, wettability appears to be an extremely sensitive analytical tool for elucidating the structure of surfaces. Wettability is quantified by the measurement of the contact angle,  $\theta$ , between the tangent to a drop of liquid where it meets the surface and the surface itself. Different liquids probe different molecular forces. Water senses primarily polar functional groups in the substrate, whereas a hydrocarbon, such as hexadecane, interacts purely by dispersive forces. Different values of the contact angle may be observed for drop edges that have advanced or receded across the surface prior to measurement. Although this hysteresis in the contact angle undoubtedly carries a wealth of structural information about the surface, no microscopic theory yet exists that explains the origin of hysteresis.

Table 1. Advancing contact angles  $\theta_a$  of water and hexadecane on monolayers of representative thiols on gold



Thiol	$\theta_a(\text{H}_2\text{O}) [^\circ]$	$\theta_a(\text{C}_{16}\text{H}_{34}) [^\circ]$
$\text{HS}(\text{CH}_2)_2(\text{CF}_2)_n\text{CF}_3$	118	71
$\text{HS}(\text{CH}_2)_n\text{-CH}_3$	112	47
$\text{HS}(\text{CH}_2)_n\text{-CH=CH}_2$	107	39
$\text{HS}(\text{CH}_2)_n\text{Br}$ [a]	97	$< 5$
$\text{HS}(\text{CH}_2)_n\text{OCOCF}_3$ [d]	96	62
$\text{HS}(\text{CH}_2)_n\text{F}$ [a]	95	$< 5$
$\text{HS}(\text{CH}_2)_n\text{Cl}$ [a]	83	$< 5$
$\text{HS}(\text{CH}_2)_n\text{OCH}_3$	75	41
$\text{HS}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$	67	28
$\text{HS}(\text{CH}_2)_n\text{CN}$ [b]	63	$< 5$
$\text{HS}(\text{CH}_2)_n\text{CONH}_2$ [c]	13	$< 5$
$\text{HS}(\text{CH}_2)_n\text{CO}_2\text{H}$	$< 10$	$< 5$
$\text{HS}(\text{CH}_2)_n\text{OH}$	$< 10$	$< 5$

From [1], except [a] B. Burbaum, unpublished results. [b] P. Laibinis, unpublished result. [c] L. Janes, unpublished result. [d] By reaction of a monolayer formed from  $\text{HS}(\text{CH}_2)_n\text{OH}$  with trifluoroacetic anhydride.

A large range of functional groups can be expressed at the surface of a monolayer of a thiol on gold. Thiols with highly polar tail groups, such as carboxylic acids, form monolayers that are wetted by water and by all non-reactive organic liquids. Fluorinated thiols form monolayers that are more water- and oil-repellent than Teflon. The hydrophobicity and oleophobicity of the surface can be varied almost independently between these two extremes (Table 1). In general, the lower the surface tension,  $\gamma_{lv}$ , of the probe liquid, the smaller the contact angle. By judicious choice of tail group, this relationship can be reversed. For example, a monolayer of  $\text{HS}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$  is wetted by acetonitrile ( $\gamma_{lv} = 29.3 \text{ mN m}^{-1}$ ;  $\theta \approx 0^\circ$ ) but not by hexadecane ( $\gamma_{lv} = 27.2 \text{ mN m}^{-1}$ ;  $\theta = 28^\circ$ ). We have, however, not yet succeeded in mimicking the unusual properties of the surface of

water itself, which is wetted by water (since any pure liquid wets itself) but not by hexadecane.

One of the key questions that we have sought to answer is how wettability is influenced by the depth of a species beneath the solid-liquid interface. The strength of the interaction between two bodies separated by a third medium can be calculated from bulk optical properties by Lifshitz theory. Given the short range of the intermolecular interactions that determine the wetting of organic surfaces, such continuum theories can at best provide only an approximate answer. Using monolayers we can tackle this problem from a molecular perspective.<sup>[4]</sup> Figure 2 plots the contact angles of

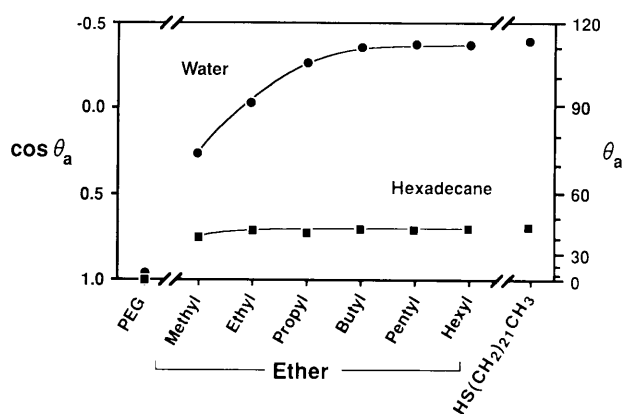


Fig. 2.  $\omega$ -Mercaptoethers,  $\text{HS}(\text{CH}_2)_{16}\text{O}(\text{CH}_2)_n\text{CH}_3$ , adsorb from ethanol onto gold and form monolayers in which the depth of the polar ether group beneath the outer surface of the monolayer increases with increasing  $n$ . The advancing contact angles  $\theta_a$  of water and hexadecane are shown as a function of the length of the terminal alkyl chain. Also shown are the contact angles on polyethylene glycol (PEG) and on a monolayer of docosane thiol on gold, models of surfaces in which ether groups are, respectively, fully exposed to the contacting liquid, and completely buried.

water and hexadecane on monolayers of ether-terminated alkanethiols,  $\text{HS}(\text{CH}_2)_{16}\text{O}(\text{CH}_2)_n\text{CH}_3$ ,  $n = 0-5$ . In this study<sup>[15]</sup> the polar ether group was buried progressively deeper beneath the monolayer-liquid interface by increasing the length of the terminal alkyl chain. The contact angles of hexadecane confirm that the dispersion interaction between the ether group and hexadecane is very short range, dropping to essentially zero when a 2 Å thickness of hydrocarbon material intervenes. Water was able to sense the polar ether group at greater depths beneath the monolayer-water interface: a butyl group was required to screen the ether oxygen fully from the supernatant drop. Similar results have been obtained using amides in place of ethers.<sup>[16]</sup> Thus we see that one only needs to control the structure of the outermost few angstroms of a smooth solid in order to determine its wetting properties. Furthermore, as an analytical technique, wettability approaches the best UHV spectroscopies in terms of surface sensitivity.

## 5. Construction of Complex Interfaces

### 5.1. Multiple Functional Groups

The ability to synthesize surfaces containing a unique functional group helps us to understand the contributions of individual chemical species to interfacial properties. Real surfaces, however, are complex both chemically and structurally. There is no a priori reason to assume that the different chemical components in an interface behave independently and hence that the properties of a multi-component surface can be inferred with confidence from the properties of surfaces composed of structured arrays of the pure components. The first step in extending our model to approximate real surfaces more closely is to introduce more than one functional group into the monolayer. To a certain extent this end can be achieved by performing reactions on the monolayer after formation. More generally, we can generate poly-functional surfaces by coadsorbing two or more thiols on gold.

In interpreting coadsorption experiments, two questions immediately present themselves. First, does the composition of the monolayer reflect the relative concentrations of the two components in solution? Second, do the different components in the monolayer phase segregate into macroscopic domains? The answer to both questions appears to be no. The composition of the monolayer is strongly influenced by interactions between the adsorbates and the solvent and among the tail groups within the monolayer. Changing the nature of the solvent, from ethanol to isooctane for example,<sup>[11]</sup> can dramatically alter the composition of a monolayer even when the concentrations in solution remain unchanged. If the adsorption components have different chain lengths, cohesive interactions between crystalline hydrocarbon chains favor incorporation of the longer chain into the monolayer. Far from merely being an inconvenience, the relationships between the composition of the monolayer and the concentrations of the adsorbates provide a handle on the molecular interactions present in the monolayer, and offer valuable insights into other processes of self-assembly, such as membrane and micelle formation.

The question of the distribution of components within the monolayer is more difficult to resolve. Although numerous pieces of evidence militate against the formation of macroscopic islands ( $\geq 1000$  Å across), the components are almost certainly not randomly dispersed, but form small clusters, as they do in solution (if by doing so the free energy is lowered). A better knowledge of the pair distribution function in these "mixed monolayers" would improve our understanding of real surfaces which, too, reconstruct to minimize their free energy.

A simple example of a mixed monolayer which displays the essential features of a coadsorption experiment is  $\text{HS}(\text{CH}_2)_{11}\text{OH}/\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  adsorbed from ethanol onto gold.<sup>[17]</sup> Figure 3A displays the relationship between the mole fraction  $\chi^{\text{OH}}$  of  $\text{HS}(\text{CH}_2)_{11}\text{OH}$  in the adsorption solu-

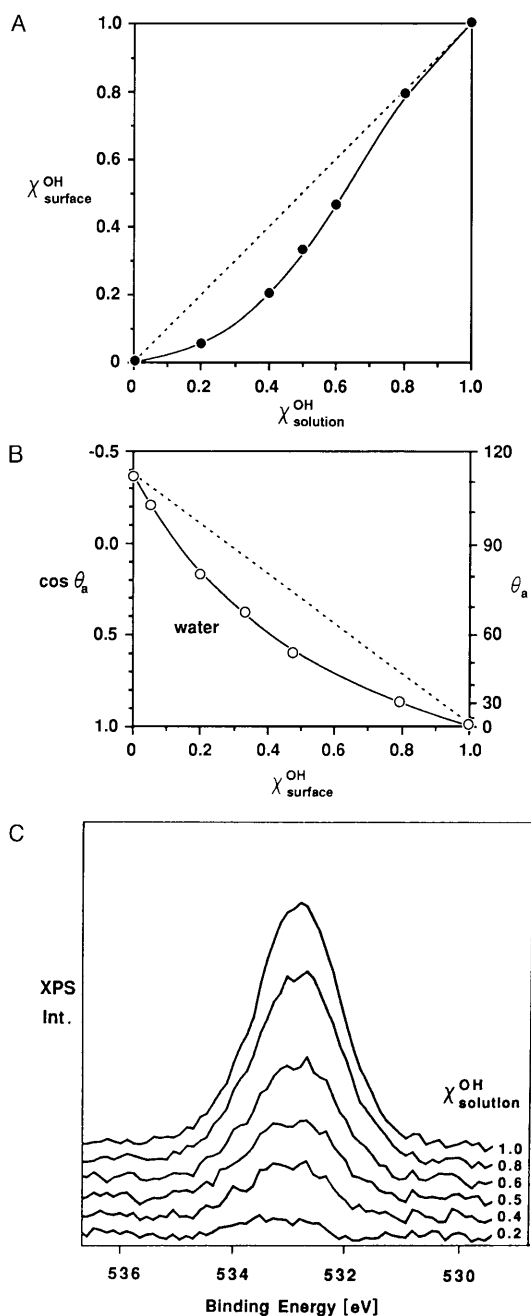


Fig. 3. Monolayers exposing both methyl and hydroxy groups at the surface of the monolayer may be formed by adsorption from solutions containing mixtures of  $\text{HS}(\text{CH}_2)_{11}\text{OH}$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ . A) Plots of the mole fraction of the hydroxy-terminated chain in the monolayer as a function of the mole fraction in solution. For clarity, the calculation of the mole fraction in solution included only the thiol species; B) plot of the advancing contact angle of water as a function of the composition of the monolayer; C) the oxygen (1s) region of the XPS spectra of the monolayers (XPS intensity in arbitrary units). The areas under these peaks were used to calculate the compositions of the monolayers.

tion and in the monolayer. The compositions of the monolayers were determined from the intensity of the O(1s) peak obtained by XPS (Fig. 3C). From solutions in ethanol there is a preference for adsorption of the methyl-terminated thiol. Adsorption of  $\text{HS}(\text{CH}_2)_{11}\text{OH}$  is particularly disfavored at low concentrations, possibly due to incomplete hydrogen-

bonding of the terminal hydroxy groups in the nonpolar environment provided by the surrounding methyl groups at the surface of the monolayer. The advancing contact angle of water is shown in Figure 3 B as a function of the mole fraction,  $\chi^{\text{OH}}$ , of the hydroxy-terminated component in the monolayer. If the wettability of a mixed monolayer were simply a linear combination of the wetting properties of the constituent components, we would expect a linear relationship between  $\cos \theta_a$  and  $\chi^{\text{OH}}$ . The actual graph is concave: the hydroxy groups at the surface of the monolayer are more hydrophilic at low  $\chi^{\text{OH}}$ , when they are in a nonpolar environment, than at high  $\chi^{\text{OH}}$ , when they are surrounded by other OH groups to which they can hydrogen bond. This result is consistent with the observed bias against adsorption of hydroxy groups at low  $\chi^{\text{OH}}$ .

Although mixed monolayers such as these may seem simple, the correlations between wettability and structure derived from such systems have proved invaluable in improving our understanding of a complex organic surface—chromic-acid-oxidized polyethylene—which contains a mixture of polar and nonpolar functionality.<sup>[18]</sup> Comparison of the polymer with mixed monolayers supported the hypothesis that the polyethylene surface was composed of domains comprising largely polar or largely nonpolar groups, rather than containing a homogeneous distribution throughout the functionalized interphase.

The principles established for simple systems composed of two thiols are readily generalizable to cases in which both thiols are terminated by complex functional groups or in which there are more than two components in the monolayer.

## 5.2. Control over Surface Disorder

Many real surfaces differ from the model monolayers discussed so far in another important respect: they are disordered. The chains and tail groups in the densely packed, oriented monolayers presented above do not have the degrees of freedom available in an amorphous polymer or a fluid biological surface. As a consequence, the monolayer cannot reconstruct in response to changes in its environment, and we cannot easily use these monolayers to study dynamic processes at interfaces. We can introduce free volume, with the conformational freedom that entails, into the outer part of the monolayer by coadsorbing two thiols with different chain lengths.<sup>[1, 19, 20]</sup> We expect the resulting mixed monolayers to have two distinct phases: the inner part, adjacent to the gold surface, remains densely packed (and hence insulates the monolayer–liquid or monolayer–air interface from the influence of the substrate), but the outer part of the monolayer contains fewer hydrocarbon chains per unit area and is free to become disordered (Fig. 4). By placing functional groups at the ends of the shorter chains, in the transition region between the ordered and disordered phases of the monolayer,<sup>[20]</sup> we can also introduce a degree

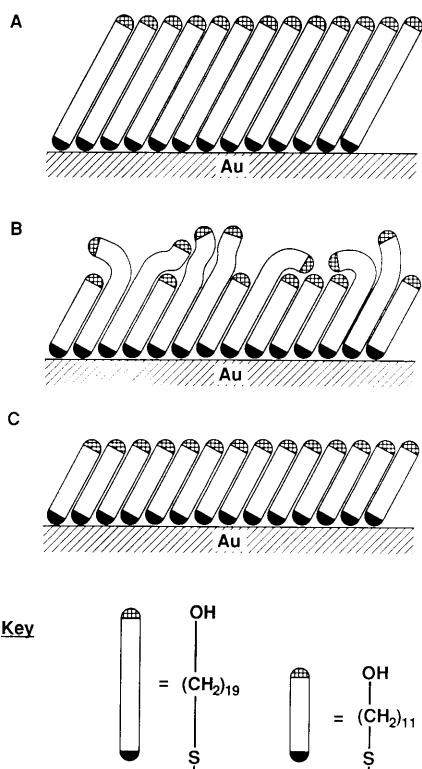


Fig. 4. Schematic illustration of monolayers of hydroxy-terminated thiols on gold. A) Pure monolayer of  $\text{HS}(\text{CH}_2)_{19}\text{OH}$ ; B) monolayer containing equal amounts of  $\text{HS}(\text{CH}_2)_{19}\text{OH}$  and  $\text{HS}(\text{CH}_2)_{11}\text{OH}$ . The inner part of the monolayer is densely packed, the outer part loosely packed and disordered; C) pure monolayer of  $\text{HS}(\text{CH}_2)_{11}\text{OH}$ .

of three-dimensionality beyond that achievable simply by varying the position of a functional group in a polymethylene chain.

The consequences of introducing disorder into the outer part of the monolayer can be seen clearly in monolayers composed of mixtures of  $\text{HS}(\text{CH}_2)_{11}\text{OH}$  and  $\text{HS}(\text{CH}_2)_{19}\text{OH}$  (Fig. 5).<sup>[19]</sup> Pure monolayers of either species expose only polar hydroxy groups at the monolayer-liquid interface and

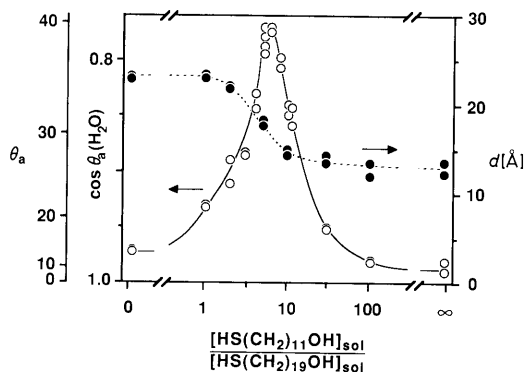


Fig. 5. Ellipsometric thickness  $d$  and advancing contact angles  $\theta_a$  of water for mixed monolayers of  $\text{HS}(\text{CH}_2)_{19}\text{OH}$  and  $\text{HS}(\text{CH}_2)_{11}\text{OH}$ . The abscissa represents the ratio of concentrations of  $\text{HS}(\text{CH}_2)_{19}\text{OH}$  to  $\text{HS}(\text{CH}_2)_{11}\text{OH}$  in solution. The maximum in contact angle correlates approximately with the monolayer shown schematically in Figure 4 B.

hence yield very low contact angles with water ( $\theta < 15^\circ$ ). In a mixed monolayer, however, the last eight carbons of the longer chains can form a disordered, liquid-like layer on top of the densely-packed lower phase of the monolayer. Since this disordered region exposes nonpolar polymethylene chains to the water drop, we expect to see a sharp increase in the contact angle (Fig. 5). The observation of just such a maximum confirms our model and rules out the formation of large, single-component domains within the monolayer: each of these domains would expose only hydroxy groups at the surface and hence the mixed monolayers would be wetted by water, independent of composition. Comparison of the contact angles in Figure 5 with those shown in Figure 3 suggests that even the most disordered mixed monolayer still exposes an approximately 2:1 ratio of polar hydroxy to non-polar methylene groups to a water drop. This ratio is not

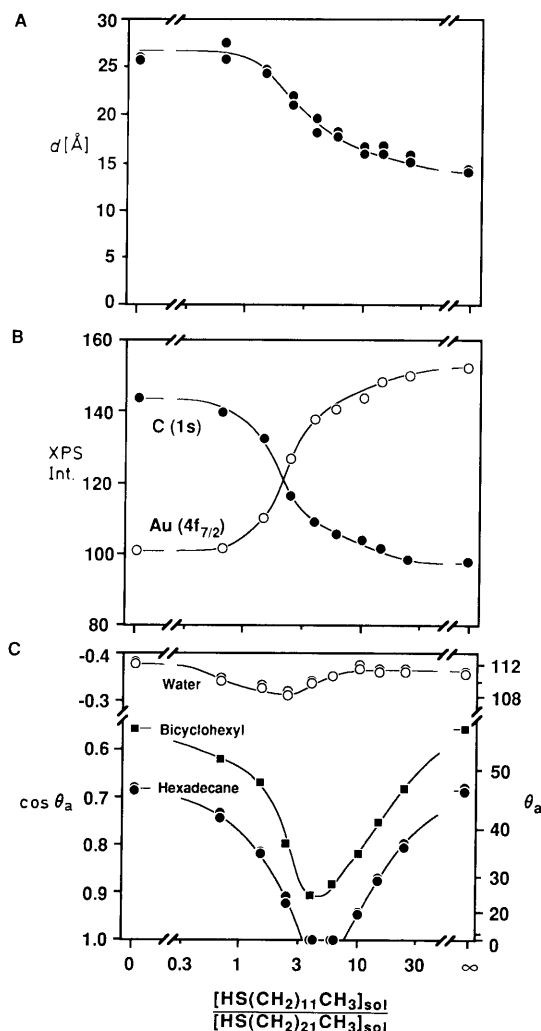


Fig. 6. Mixed monolayers formed by coadsorption of  $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$  from isoctane. The abscissa represents the ratio of concentrations of  $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$  to  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$  in solution. A) Ellipsometric thickness of the monolayers; B) intensity of the C(1s) and Au(4f<sub>7/2</sub>) peaks obtained by XPS (arbitrary units): The compositions of the monolayers can be calculated from the intensities of these peaks. C) Advancing contact angles of water, hexadecane and bicyclohexyl.

unreasonable. We would expect the monolayer to reconstruct to maximize hydrogen-bonding and to minimize the number of hydrophobic contacts.

If the two thiols are terminated by methyl groups instead of hydroxy groups, then the resulting mixed monolayers allow us to probe the effect of local structure on dispersive interactions and on the hydrophobic effect. Figure 6 shows the ellipsometric thickness  $d$ , XPS intensities and contact angles  $\theta_a$  for monolayers adsorbed from mixtures of  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$  in isoctane. (The first two techniques serve to establish the composition of the monolayer.) Pure monolayers of either component expose a densely packed array of methyl groups at the surface of the monolayer, and are both hydrophobic and oleophobic. The surface of a monolayer containing an approximately equal mixture of the two components resembles a liquid, linear hydrocarbon. The advancing contact angle of water  $\theta_a$  is insensitive to the detailed structure of the hydrocarbon surface. On the other hand, hydrocarbon liquids, such as bicyclohexyl and hexadecane, show large changes in contact angle in response to variations in the structure of the surface. A corollary of these observations is that variations in the strength of the hydrophobic effect arise largely from hydrocarbon-hydrocarbon interactions rather than hydrocarbon-water interactions. There is also some evidence<sup>[1]</sup> that decane can penetrate into holes left in a monolayer of  $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$  by the presence of molecules of  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ —a primitive type of molecular recognition.

## 6. Concluding Remarks

We can only arrive at a detailed understanding of the complex physical and chemical properties of surfaces through the study of well-defined model systems. Phenomena such as wetting, adhesion, and friction are all functions (albeit complicated ones) of the microscopic chemical structure of a surface. Self-assembled monolayer films of thiols on gold are model systems in which the microscopic structural attributes of an organic surface can be varied independently and the influence on interfacial properties determined. We believe that they, and other related systems, will provide the bridge between the physical-organic chemistry of solutions and the materials science of organic solids. The research presented here is only a first step towards developing an

understanding of organic surfaces. We still have to learn more about measuring and controlling the lateral distribution of functional groups. Many interesting features of wetting—especially the influence of roughness and chemical heterogeneity, and the origin of hysteresis—are still not understood. We have barely touched upon interfacial properties other than wetting, such as adhesion, friction and electrochemistry. Much remains to be learned about the physical-organic chemistry of condensed interphases.

Self-assembled monolayers are more than mere model systems for the surfaces of materials. They provide a starting point for practical technologies to solve interfacial problems. Two examples are the use of monolayers of alkylsiloxanes to promote adhesion or, with the opposite intent, to prevent catalyst particles from sticking to the walls of reactors. The intermolecular interactions controlling the structure of self-assembled monolayers are also acting in other spontaneously assembling systems. In studying them we will learn more about membranes, micelles and microemulsions.

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- [1] C. D. Bain, *PhD Thesis*, Harvard University 1988; G. S. Ferguson, G. M. Whitesides, *Chemtracts* 1 (1988) 171.
- [2] J. Sagiv, *J. Am. Chem. Soc.* 102 (1980) 92.
- [3] See, for example, a recent review: H. Möhwald, *Angew. Chem. Adv. Mater.* 100 (1988) 750; *Angew. Chem. Int. Ed. Engl. Adv. Mater.* 27 (1988) 728.
- [4] For a review of early work on self-assembled monolayers, see W. A. Zisman in F. M. Fowkes (Ed.): *Contact Angles, Wettability, and Adhesion* (*Adv. Chem.* 43) American Chemical Society, Washington, DC 1964, pp. 1–51.
- [5] S. R. Wasserman, G. M. Whitesides, I. M. Tidswell, B. M. Ocko, P. S. Pershan, J. D. Axe, *J. Am. Chem. Soc.*, in press; S. R. Wasserman, Y.-T. Tao, G. M. Whitesides, *Langmuir*, in press.
- [6] N. Tillman, A. Ulman, T. L. Penner, *Langmuir*, in press.
- [7] L. Netzer, R. Iscovici, J. Sagiv, *Thin Solid Films* 99 (1982) 235.
- [8] R. G. Nuzzo, D. L. Allara, *J. Am. Chem. Soc.* 105 (1983) 4481.
- [9] C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.* 111 (1989) 321.
- [10] M. D. Porter, T. B. Bright, D. L. Allara, C. E. D. Chidsey, *J. Am. Chem. Soc.* 109 (1987) 3559.
- [11] R. G. Nuzzo, L. H. Dubois, D. L. Allara, *J. Am. Chem. Soc.*, in press.
- [12] L. Strong, G. M. Whitesides, *Langmuir* 4 (1988) 546.
- [13] C. D. Bain, G. M. Whitesides, *J. Phys. Chem.*, in press.
- [14] P. G. DeGennes, *Rev. Mod. Phys.* 57 (1985) 827; J. N. Israelachvili: *Intermolecular and Surface Forces*, Academic Press, London 1985.
- [15] C. D. Bain, G. M. Whitesides, *J. Am. Chem. Soc.* 110 (1988) 5897.
- [16] B. Burbaum, I. Janes, G. M. Whitesides, unpublished results.
- [17] C. D. Bain, G. M. Whitesides, *J. Am. Chem. Soc.* 110 (1988) 6560.
- [18] S. R. Holmes-Farley, C. D. Bain, G. M. Whitesides, *Langmuir* 4 (1988) 921.
- [19] C. D. Bain, G. M. Whitesides, *Science (Washington, D.C.)* 240 (1988) 62.
- [20] C. D. Bain, G. M. Whitesides, *J. Am. Chem. Soc.* 110 (1988) 3665.

### The following review article will appear in future issues:

*D. W. McCall*: Materials Issues in Electronic Systems. *W. Michaeli*: Material Processing—a Key Factor. *B. R. Phillips*, *D. Tanner*, *J. A. Fitzgerald*: The Kevlar Story—An Advanced Materials Case Study. *M. Salkind*: Aerospace Materials Research Opportunities. *D. F. Williams*: Challenges in Materials for Health Care Applications. *T. Kodas*: Aerosol/Processing of Complex Metal Oxides. *H. Warlimont*: Rapidly Quenched Materials. *H.-W. Schmidt*: Dichroic Dyes and Liquid Crystalline Side Chain Polymers.