

(3.77 d, d, 2 H,  $J = 5.4$  Hz), 4.24 (t, 1 H,  $J = 5.4$  Hz), 7.49 (m, 9 H), 8.01 (m, 4 H), 8.29 (m, 2 H). MS (EI):  $m/e$  354 ( $M^+$ ). MS (FAB):  $m/e$  355 ( $M^+ + 1$ ). The yields of the products were determined by  $^1\text{H}$  NMR spectroscopy to be **4** (52%), **1** (26%), and benzyl methyl sulfide (18%).

**Sensitization of IMSY.** A  $7.5 \times 10^{-3}$  M solution of the ylide in 20 mL of DCA-saturated acetonitrile was irradiated for 6 h. Evaporation of the solvent gave an orange solid. Its  $^1\text{H}$  NMR spectrum revealed residual ylide and compounds **4** and **5**. The products were identified by GC/MS analysis and isolated by radial chromatography. The products yields were determined by  $^1\text{H}$  NMR spectroscopy to be 38% **4** and 10% **5** at 30% conversion of IMSY.

**Sensitization of DMSY, EMSY, TMSY, and BTSY.** Solutions of the ylides ( $7.5 \times 10^{-3}$  M in 20 mL of DCA-saturated acetonitrile) were irradiated. Evaporation of solvent in each case gave an orange solid. Analysis by  $^1\text{H}$  NMR spectroscopy and GC/MS revealed residual ylide and formation of cyclopropane **1**: formed in 91% yield at 30% conversion from DMSY, 82% yield at 31% conversion from EMSY, 85% yield at 31% conversion of TMSY, and 65% yield at 33% conversion of BTSY. In this case, 2,7-dihydrobenzothiophene was formed in 33% yield.

**Sensitization of BMSY in the Presence of Tetra-*n*-butylammonium Acetate.** A  $5 \times 10^{-3}$  M solution of BMSY in 20 mL of DCA-saturated acetonitrile containing  $5 \times 10^{-3}$  M tetra-*n*-butylammonium acetate was placed in a Pyrex vessel and purged with nitrogen for 30 min. The sample was irradiated ( $\lambda > 400$  nm) for 10 h. Evaporation of solvent

gave an orange solid.  $^1\text{H}$  NMR spectral analysis of the crude product revealed residual BMSY, **4**, **1**, and 2-acetoxyacetophenone: mp 44–45 °C, identified by comparison with an authentic sample.

**Sensitization of DMSY in the Presence of Isobutene.** Isobutene was bubbled into a  $5 \times 10^{-3}$  M solution of BMSY in 18 mL of DCA-saturated acetonitrile (0 °C) in a Pyrex vessel until the solution volume had increased by ca. 2 mL. The vessel was sealed and irradiated ( $\lambda > 400$  nm) for 8 h. The  $^1\text{H}$  NMR spectrum and a GC/MS analysis of the crude product revealed residual DMSY, cyclopropane **1**, and a new product identified as 4,4-dimethyl-1-tetralone (**2**) based on its spectral properties and the preparation of a derivative:<sup>26</sup>  $^1\text{H}$  NMR:  $\delta$  1.396 (s, 6 H), 2.02 (t, 2 H,  $J = 7$  Hz), 2.74 (t, 2 H,  $J = 7$  Hz), 7.28–7.52 (m, 3 H), 8.02 (d, 1 H). GC/MS:  $m/e$  174 ( $M^+$ ), 159, 131, 91.

The 2,4-dinitrophenylhydrazone of **2** was prepared and recrystallized from ethyl acetate: mp 121–125 °C (lit.<sup>27</sup> 125–126 °C).  $^1\text{H}$  NMR:  $\delta$  1.36 (s, 6 H), 1.96 (t, 2 H,  $J = 7$  Hz), 2.86 (t, 2 H,  $J = 7$  Hz), 7.42 (m, 2 H), 8.20–8.46 (m, 4 H), 9.18 (d, 1 H) MS (FI):  $m/e$  354 ( $M^+$ ).

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## Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Head Group, Tail Group, and Solvent<sup>1</sup>

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**Abstract:** Long-chain alkanethiols,  $\text{HS}(\text{CH}_2)_n\text{X}$ , adsorb from solution onto gold and form oriented, ordered monolayers. Monolayers exposing more than one functional group at the surface can be generated by coadsorption of two or more thiols from solution. In general, the ratio of the concentration of the two components in a mixed monolayer is not the same as in solution but reflects the relative solubilities of the components in solution and interactions between the tail groups, X, in the monolayers. Multicomponent monolayers do not phase-segregate into single-component domains large enough to influence the contact angle (a few tens of angstroms across) and also do not act as ideal two-dimensional solutions. In the two-component system  $\text{HS}(\text{CH}_2)_n\text{X}/\text{HS}(\text{CH}_2)_n\text{CH}_3$  in ethanol, where X is a polar tail group such as  $\text{CH}_2\text{OH}$  or CN, adsorption of the polar component is particularly disfavored at low concentrations of the polar component in the monolayer. These isotherms may arise from poor solvation of the polar tail groups in the quasi-two-dimensional alkane solution provided by the methyl tail groups. From dilute solutions in alkanes, adsorption of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  is strongly preferred over  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ , probably due to the stabilization afforded by intramonolayer hydrogen bonds between the hydroxyl tail groups. The wettability of mixed monolayers is not linear in the composition of the surface. In a surface comprised of a polar and a nonpolar component, the polar component is more hydrophilic when its concentration in the monolayer is low than when the monolayer is composed largely of the polar component.

The formation of oriented monolayer films on a surface by the spontaneous adsorption of molecules from solution has become known as self-assembly. Of all the types of self-assembled monolayers that have been studied,<sup>3</sup> two systems have shown the greatest promise as a means of controlling the chemical structure

of organic surfaces: adsorption of organosulfur compounds on noble metals such as gold<sup>4–8</sup> and silver,<sup>9</sup> and reaction of alkyl-trichlorosilanes with silicon or glass.<sup>10</sup> Our research has concentrated on the first of these systems.<sup>11</sup> In a previous paper,<sup>8</sup> we presented a study of the formation, characterization, and properties of monolayers generated by the adsorption of *n*-alka-

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nethiols,  $\text{HS}(\text{CH}_2)_n\text{X}$ , on gold. In these monolayers, the chemistry, structure, and properties of the surface were controlled by varying the tail group, X. The range of properties that can be obtained in homogeneous monolayers of a single thiol is, however, limited. Greater control over the structure of the monolayer is afforded by coadsorption of two or more thiols that differ in the nature of the tail group<sup>12</sup> or the length of the hydrocarbon chain.<sup>13</sup> This paper is the first of two that examine monolayers formed by the coadsorption of two species that differ in the chain length, the tail group, or the nature of the head group that binds the components of the monolayer to the gold surface.

In this paper, we present a brief survey of organic functional groups, other than thiols, that coordinate to gold and form stable monolayers. Then we examine monolayers formed from mixtures of two thiols with the same chain length but with different tail groups. Finally, we address the effect of solvent on the composition of the monolayers and its implications for the mechanism of adsorption. In the companion paper, we discuss mixed monolayers composed of two thiols having different chain lengths.<sup>14</sup>

We had three broad aims in this study. First, we wished to understand how the composition of a monolayer is related to the relative concentrations of thiols in the adsorption solution and, in particular, whether the formation of monolayers is under kinetic or thermodynamic control. If the monolayers are in thermodynamic equilibrium with the adsorption solutions, it should be possible to derive thermodynamic properties of the monolayers from the adsorption isotherms. A quantitative analysis of the adsorption isotherms is beyond the scope of these papers. Here we discuss qualitatively the impact of excess entropy and enthalpy on the composition of the monolayers.<sup>15</sup>

Second, we wished to elucidate the structure of the mixed monolayers. In particular, we wanted to establish whether the two components in the monolayer segregate into macroscopic, single-component domains and, if not, to what extent the components do aggregate into small clusters on the surface.<sup>16</sup> In this context, we use "macroscopic" to mean sufficiently large such that the properties of the monolayer are dominated by molecules that are in an environment indistinguishable from that in a pure (i.e., single-component) monolayer. In the absence of long-range electrostatic interactions, macroscopic probably applies to islands more than a few tens of angstroms across. We will present the data in this paper under the assumptions that thermodynamics controls the composition of the mixed monolayers and that the monolayers are not phase-segregated and then discuss the evidence that lends support to these assumptions. We will also try to define more closely the extent of aggregation of the two components in the monolayer.

Third, we wished to investigate how the macroscopic physical properties of an interface—particularly the wettability—are related to the microscopic chemical structure of the surface.

The general strategy in these studies was to prepare solutions containing two thiols,  $\text{HS}(\text{CH}_2)_n\text{X}$  and  $\text{HS}(\text{CH}_2)_m\text{Y}$  differing in the nature of the tail group (X, Y) and/or the chain length (*m*, *n*), in a range of mole fractions but with the same total concentration of thiol moieties in solution. Gold slides were immersed in these solutions overnight under ambient conditions of temperature and pressure. The formation of strong, coordinative gold-sulfur bonds drives the spontaneous assembly of the monolayers. We then used ellipsometry and X-ray photoelectron spectroscopy (XPS) to determine the composition of the monolayer

and used contact angles,  $\theta$ , to measure its wettability.

We believe<sup>8,17,18</sup> that the species ultimately formed on the gold surface by adsorption of thiols from solution is a thiolate ( $\text{Au-SR}$ ). The mechanism by which an initially physisorbed thiol is converted to a chemisorbed thiolate remains unclear. In this paper, we will use phrases such as "monolayer of an alkanethiol" to indicate the precursor from which the monolayer was formed, even though the actual species at the gold surface is probably a thiolate. We will designate monolayers adsorbed from pairs of thiols as X/Y to indicate the pair of tail groups, X and Y, that are exposed at the surface of the monolayers. Thus, for example, the monolayer prepared by adsorption of thiols from a solution containing  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  would be designated OH/Me. We will also use terms such as "methyl surface" to refer to the surface of a monolayer that exposes primarily methyl groups at the monolayer-air or monolayer-liquid interface.

In these papers, we generally plot contact angles on axes that are linear in  $\cos \theta$ , not in  $\theta$  itself.  $\cos \theta$  is related to surface free energies through Young's equation<sup>19</sup>

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

where  $\gamma_{lv}$ ,  $\gamma_{sv}$ , and  $\gamma_{sl}$  are the liquid-vapor, solid-vapor, and solid-liquid surface free energies, respectively. Changes in  $\cos \theta$  are thus linearly related to the changes in interfacial free energies. In general,  $\cos \theta$  is not linearly dependent on the composition of the surface,<sup>20</sup> and hence contact angles cannot easily be used for quantitation. Contact angles do provide structural information about the surface of a monolayer. The contact angle of water is sensitive to the polarity of the surface; the contact angle of hexadecane reflects the polarizability and, as we shall show, the degree of order in the surface. The contact angle of water is more sensitive than the contact angle of hexadecane to the presence of polar functional groups buried below the monolayer-liquid interface.<sup>21</sup> A comparison of the contact angles of water and hexadecane can thus provide considerable insight into the three-dimensional structure of a monolayer. Hysteresis in the contact angle also carries valuable structural information, but its interpretation is not well-understood. In this paper, we express the hysteresis in the contact angle as the difference between the minimum receding contact angle and the advancing contact angle, expressed as cosines:  $\cos \theta_r - \cos \theta_a$ .<sup>22</sup>

**Thermodynamic versus Kinetic Control over the Formation of Monolayers.** One of the enigmas in these studies, which we have not yet fully resolved, is whether the composition of a monolayer adsorbed from a solution containing two or more thiols is determined by equilibration between the components in the monolayer and the precursors to the monolayer in solution or by the kinetics of adsorption. This question is complicated by experimental observations that, at first sight, are mutually inconsistent. Most of the data in this and the following paper can be rationalized if the compositions of the mixed monolayers were at, or near, the values we would expect from thermodynamic equilibrium between the components of the monolayer and the adsorption solutions. It is difficult to construct a purely kinetic mechanism that accounts for the observed compositions. For example, a monolayer adsorbed from a mixture of two linear thiols with the same chain length may be composed almost exclusively of the minor species in solution, even when there is no obvious kinetic preference for one

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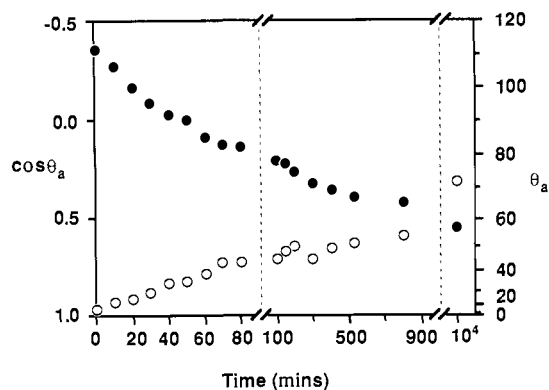
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**Figure 1.** Displacement of monolayers of thiols on gold. Advancing contact angle of water as a function of the time of immersion of a preformed monolayer of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  in a 1 mM solution of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  in ethanol (filled circles) and of a preformed monolayer of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  in a 1 mM solution of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  in ethanol (open circles). Note the change in the scale of the abscissa after 100 min and the axis break after 900 min.

species over the other. Similarly, long-chain thiols were adsorbed preferentially over shorter chains, a preference that is antithetical to our intuition based on relative diffusion rates and steric hindrance. The presumption of thermodynamic equilibrium requires that a mechanism exist for reversible interchange of the components of the monolayer with those in solution at some time during the formation of the monolayer. Here a problem arises. The rate of desorption of molecules into solution from fully formed monolayers at room temperature is negligible, so equilibrium cannot be established by desorption and re-adsorption of monolayer components in the complete monolayer. Similarly, displacement of components in a preformed monolayer by thiols in solution (Figure 1) is too slow to account for the rapid equilibration (within, at most, a few seconds) required to explain the experimental results: after 12 h of immersion in a 1 mM solution of  $\text{HS}(\text{CH}_2)_{10}\text{X}$ , less than half of a preformed monolayer of  $\text{HS}(\text{CH}_2)_{10}\text{Y}$  ( $\text{X}, \text{Y} = \text{CH}_3, \text{CH}_2\text{OH}$  and vice versa) had been replaced by  $\text{HS}(\text{CH}_2)_{10}\text{X}$ . With monolayers composed of longer chains, displacement was even slower.

This apparent paradox could be resolved if rapid equilibration were to occur at short times through some mechanism that was not available in the fully formed monolayer. One can postulate several possibilities. First, equilibration could proceed through the physisorbed thiol. Rapid equilibration between the physisorbed thiol and the thiols in solution would be followed by relatively slow conversion of the physisorbed thiols to chemisorbed thiolates. If the rate constant for the conversion of thiol to surface thiolate were independent of the structure of the thiol, which is likely, a chemisorbed monolayer would be kinetically trapped with a composition equal to the equilibrium value in the physisorbed monolayer. Thus, even if the fully formed monolayer did not equilibrate with the components in solution, equilibration through the physisorbed thiol could result in an equilibrium composition of the components in the monolayer. This mechanism is consistent with the observation that the activation barrier in UHV to desorption of a physisorbed thiol is lower than the barrier to chemisorption.<sup>18</sup> Second, equilibration during the early stages of monolayer formation could also conceivably proceed through the adsorbed thiolate. For example, the presence of surface hydrides (formed by dissociative chemisorption of the thiol) might be required for reversible adsorption. Surface hydrides would be lost rapidly as  $\text{H}_2$ <sup>23</sup> or  $\text{H}_2\text{O}$ , shutting down this mechanism and freezing in the equilibrium composition. Third, exchange between the monolayer and the solution is somehow mediated by unoccupied coordination sites on the gold. Clearly, it is important to determine the mechanism of adsorption and equilibration during the early stages of formation of a monolayer. As yet, however,

we do not have firm evidence to support a particular mechanism, and we prefer not to speculate further.

## Experimental Section

**Materials.** Ethanol (U.S. Industrials Co.) was deoxygenated with nitrogen before use. Hexadecane (Aldrich, 99%), bicyclohexyl (Aldrich, 99%), decane (MCB), and isooctane (Fluka, HPLC grade) were slowly percolated twice through neutral, grade 1 alumina. Hexadecane and bicyclohexyl passed the Bigelow test.<sup>24</sup> Acetonitrile (Aldrich, gold label) was stirred over neutral, grade 1 alumina for 1 day and then distilled from calcium hydride.  $\alpha$ -Bromonaphthalene (Aldrich, 98%) was passed through silica gel and distilled from  $\text{P}_2\text{O}_5$  in vacuo. Water was deionized and then distilled in a glass and Teflon still. Octylisocyanide (Dixon Fine Chemicals) was purified by flash chromatography on silica gel. Trioctylphosphine (Aldrich) was distilled in vacuo and stored under  $\text{N}_2$ . 11-Mercaptoundecanol, bis(11-hydroxyundecyl) disulfide, diundecyl disulfide, 11-mercaptoundecanoic acid, 11-bromoundecanethiol, 9-mercaptanonanethiol, nonanethiol, undecanethiol, dodecanethiol, hexadecanethiol, nonadecanethiol, and docosanethiol were available from previous studies.<sup>6,8</sup> 19-Mercapto-1-nonadecanol was synthesized by coupling of 1,8-dibromooctane and 11-undecenylmagnesium bromide with catalytic  $\text{Li}_2\text{CuCl}_4$ , conversion of the terminal vinyl group to a terminal hydroxyl group with disiamylborane followed by alkaline hydrogen peroxide, conversion of the bromide to the thioacetate with thioacetic acid, and hydrolysis in acidic methanol to yield the thiol. Details may be found in the supplementary material.

**Preparation of Gold Substrates.** A thermal evaporator operating at  $10^{-6}$ – $10^{-7}$  Torr was used to deposit 50 Å of chromium and 1000–2000 Å of gold (99.99%) onto polished (111) silicon wafers (Monsanto). The wafers were stored in polypropylene containers (Fluoroware) and cut into smaller slides (1 cm  $\times$  3 cm) before use.

**Formation of Monolayers.** Glassware was cleaned by heating for 1 h in "piranha" solution (7:3 concentrated  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2$  at 90 °C) followed by exhaustive rinsing with distilled water, a final rinse with absolute ethanol, and drying in an oven. *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care.* Adsorption solutions containing two thiols were prepared in glass weighing bottles by diluting 4 mM stock solutions from 25-mL volumetric flasks. The accuracy of the concentrations of the stock solutions was limited by the analytical balance used to weigh the solid adsorbates: estimated limits of error equal  $\pm 5\%$ . The transfers were carried out in gas-tight syringes under air. The transfer procedure may introduce errors up to  $\pm 0.01$  in the mole fraction. The total concentration of thiol in solution was 1 mM. In solutions containing disulfides, each molecule of the disulfide was counted twice so that the total concentration of sulfur-terminated alkyl chains in solution was 1 mM. Fresh solutions were always employed. Gold slides were washed with ethanol, blown dry with a stream of argon, and immersed in the solutions overnight at room temperature.

**Ellipsometry.** Ellipsometric measurements were made on a Rudolf Research Type 43603-200E ellipsometer using a wavelength of 6328 Å (He-Ne laser) and an incident angle of 70°. Details of the measurement procedure have been given previously.<sup>6</sup> The observed scatter in the data was typically  $\pm 2$  Å, arising largely, we believe, from differences in the amount of adventitious material adsorbed on the bare gold substrates before formation of monolayers.

**Contact Angles.** Contact angles were determined by the sessile drop technique on a Ramé-Hart Model 100 goniometer at room temperature and 100% relative humidity for water and ambient humidity for other liquids. Advancing contact angles,  $\theta_a$ , were measured by forming a 1- $\mu\text{L}$  drop (2  $\mu\text{L}$  for angles over 80°) at the end of a PTFE-coated, blunt-ended needle, lowering the drop to the surface and removing the needle. Maximum advancing and minimum receding contact angles were measured using the technique of Dettre and Johnson.<sup>25</sup>

**X-ray Photoelectron Spectroscopy.** XPS spectra were obtained on an SSX-100 spectrometer (Surface Science Instruments) equipped with an Al K $\alpha$  source, quartz monochromator, concentric hemispherical analyzer operating in fixed analyzer transmission mode, and multichannel detector. The take-off angle was 35°, and the operating pressure was about  $10^{-9}$  Torr. Acquisition times were sufficiently short that errors due to X-ray-induced damage were small.<sup>7</sup> The seven or eight samples in each experiment were mounted simultaneously on a multisample stage and analyzed sequentially using the automatic rotation facility. Samples were not focused individually. Variations in the vertical position of the sample with respect to the focal plane of the spectrometer introduced a random

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error into the peak areas of approximately 3%. All spectra were referenced to Au(4f<sub>7/2</sub>) at 84.00 eV. Spectra of O(1s), N(1s), and Br(3p<sub>3/2</sub>) used to quantitate the composition of the monolayer were acquired with a 100-eV pass energy, 1-mm spot size, 200-W anode power, and 15–30 scans (approximately 20–40-min acquisition time). The O(1s), N(1s), and Br(3p<sub>3/2</sub>) signals were fitted with single 80% Gaussian/20% Lorentzian peaks, which were good approximations to the peak shapes on the monolayers with  $\chi^2 = 1.0$ . To calculate the composition of the monolayer, the area of the residual signal (if any) from the heteroatom on the pure methyl-terminated monolayer was subtracted from the areas of the peaks from the monolayers containing the heteroatom. These areas were normalized to the corrected area from the pure monolayer derived from HS(CH<sub>2</sub>)<sub>n</sub>X. The amount of oxygen, nitrogen, or bromine in the monolayer can also be determined by subtracting the spectrum obtained on the pure methyl-terminated monolayer from the other spectra before fitting the peaks. This procedure leads to a flat base line, which aids background subtraction, but also increases the noise by 40% and hence increases the fitting errors. Compositions calculated by this technique for the OH/Me monolayers adsorbed from ethanol agreed to within 2% of a monolayer with those calculated from the unsubtracted peaks. The Au(4f) photoelectrons were detected under the same conditions as the heteroatoms but with only two scans. Both peaks were fit by using a Shirley background subtraction<sup>26</sup> and a 80% Gaussian/20% Lorentzian peak shape, but only the area of the Au(4f<sub>7/2</sub>) peak was used for quantitation.

The random error in data acquisition and peak fitting was determined for monolayers adsorbed from a typical solution of 0.6 mM HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH and 0.4 mM HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> in ethanol. Eight gold slides adsorbed from the same solution were analyzed sequentially by using a multisample stage under the same conditions used in the analysis of a series of samples of varying composition. The standard error in both the O(1s) intensity and O/Au ratio was 3%. The O(1s) and Au(4f<sub>7/2</sub>) intensities were partially correlated as expected if differences in the focus of the samples were a cause of variability in the measured areas of the photoelectron peaks. The two samples that had the highest O(1s) intensities also had the highest Au(4f<sub>7/2</sub>) photoelectron intensities. The compositions of the monolayers presented in subsequent figures were calculated from the intensity of the O(1s), N(1s), or Br(3p) photoelectron. On one occasion in which the Au(4f<sub>7/2</sub>) intensity was abnormally low (>3 $\sigma$  deviation from the mean of the other samples within an experiment), the intensity of the photoelectrons from the heteroatom was corrected for the deviation in the gold intensity. This case arose in the Br/Me system, in which there was no plausible cause of the aberration other than instrumental factors.

## Results

**Coordination to Gold.** Potential head groups can be divided into two broad categories: those that contain sulfur and those that do not. We have surveyed a number of long-chain compounds in the second category for their ability to form monolayers on gold from dilute solutions in ethanol (with the exception of trihexadecylphosphine, which was adsorbed from acetonitrile). The rationale for this survey was partly to find other stable monolayer systems and partly to determine whether particular tail groups are likely to compete strongly with a thiol in binding to the gold. Our criteria were that the monolayers be stable to washing with ethanol and have advancing contact angles,  $\theta_a$ , that are indicative of a relatively well-packed monolayer: for long-chain, methyl-terminated adsorbates,  $\theta_a(\text{H}_2\text{O}) > 100^\circ$  and  $\theta_a(\text{HD}) > 40^\circ$ . Stearamine, heptadecanol, stearic acid,<sup>27</sup> stearamide, stearonitrile, 1-bromodocosane, ethyl hexadecanoate, and didodecylmercury did not meet these criteria (see supplementary material for details). Tricosylisonitrile formed a stable monolayer with a thickness (30 Å) close to that expected for a monolayer oriented approximately normal to the surface, but the contact angles of water and hexadecane (102° and 28°, respectively) were substantially lower than on monolayers of alkanethiols (112° and 47°). Of the molecules surveyed, only trihexadecylphosphine passed all these tests ( $\tau = 21$  Å,  $\theta_a(\text{H}_2\text{O}) = 111^\circ$ ,  $\theta_a(\text{HD}) = 44^\circ$ ). The phosphorus signal in XPS was too weak to be observed in this monolayer. In a monolayer of trioctylphosphine, an unresolved doublet arising from the P(2p) photoelectrons was observed at a binding energy of 131.7 eV,<sup>28</sup> confirming the presence of a phosphine in the monolayer.<sup>29</sup>

Competitive adsorption of a thiol and a trialkylphosphine or an alkylisonitrile indicated that adsorption of a thiol is strongly preferred over an isonitrile but showed no strong preference between a thiol and a phosphine (see supplementary material for details).

Given that “soft” nucleophiles such as phosphines and isonitriles coordinate to gold, it is not surprising that sulfur also binds well. The formation of self-assembled monolayers has been reported for several sulfur-containing molecules<sup>30</sup> other than thiols, including disulfides (RSSR),<sup>4,31</sup> sulfides (RSR),<sup>6,32</sup> and thiophenes.<sup>33</sup> There exists some disagreement over the relative binding efficiencies of thiols and dialkyl sulfides. Troughton et al.<sup>6</sup> reported that, when a dilute solution of a dialkyl sulfide in ethanol was doped to the extent of 1% with a thiol, a monolayer adsorbed from the solution had the same properties as a monolayer formed in a solution of the pure thiol. Monolayers of dialkyl sulfides were also thermally less stable than monolayers derived from thiols. These observations suggest that adsorption of thiols is strongly preferred over adsorption of sulfides. Rubenstein et al.<sup>34</sup> assumed, from indirect electrochemical evidence, that the composition of a monolayer adsorbed on a gold electrode from a solution containing an equimolar mixture of an alkylthiol and a dialkyl sulfide reflected the composition of the solution. The actual composition of the monolayer was not determined, however, and the contact angles reported in the paper suggest that the monolayer consisted primarily of the thiol component.

We have studied the relative binding efficiencies of thiols and disulfides by adsorbing monolayers from solutions containing various mole fractions of HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH and [S(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>]<sub>2</sub> in ethanol. The experiment was repeated with HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> and [S(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH]<sub>2</sub> to enable us to eliminate the influence of the tail group on the adsorption process. The results (see supplementary material for details) indicated that adsorption of the thiol was preferred over the disulfide by 2 orders of magnitude.<sup>17</sup>

### Competitive Adsorption of Thiols with Different Tail Groups.

To investigate the effect of the nature of the tail group on the coadsorption of thiols, we studied four two-component systems, each composed of a methyl-terminated thiol and a thiol with a polar or polarizable tail group. Two of the tail groups were polar and capable of intramonolayer hydrogen bonding (alcohol and carboxylic acid), one was dipolar aprotic (nitrile), and one was a highly polarizable group that does not form hydrogen bonds (bromide): HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> and HS(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H; HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> and HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH; HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> and HS(CH<sub>2</sub>)<sub>8</sub>CN. For each pair of compounds, a series of solutions were prepared in ethanol with a total concentration of 1 mM and varying mole fractions of the two components. Gold slides were immersed in these solutions overnight at room temperature, and the monolayers were then analyzed by XPS and contact angle.

The compositions of the monolayers were determined from the intensity of the photoelectron signal from the heteroatom in the tail group (O, N, or Br), normalized to the intensity from the monolayers composed solely of the thiol with a polar tail group.<sup>35</sup>

(28) For comparison, [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>3</sub>Pt gives rise to a P(2p) signal at 131.4 eV (Riggs, W. M. *Anal. Chem.* **1972**, *44*, 830).

(29) It is likely that some other trivalent phosphorus compounds (such as phosphalkynes: Kool, L. B., unpublished results) also coordinate to gold.

(30) Surprisingly, octadecyl isothiocyanate and ammonium dodecylthiocarbamate did not yield high-quality monolayers (Laibinis, P., unpublished results). Sodium hexadecyl xanthate did, however, form a monolayer ( $\tau = 21$  Å,  $\theta_a(\text{H}_2\text{O}) = 108^\circ$ ,  $\theta_a(\text{HD}) = 45^\circ$ ).

(31) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358–2368.

(32) Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107–6108.

(33) Li, T. T.-T.; Liu, H. Y.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 1233–1239.

(34) Rubenstein, I.; Steinberg, S.; Tor, Y.; Shanzer, A.; Sagiv, J. *Nature* **1988**, *332*, 426–429. Monolayers were formed from solutions containing 20 mM octadecanethiol and 20 mM 2,2'-thiobis(ethyl acetoacetate) in 4:1 bicyclohexyl/chloroform. Contact angles of  $\theta_a(\text{H}_2\text{O}) = 108^\circ$ ,  $\theta_a(\text{bicyclohexyl}) = 59^\circ$ , and  $\theta_a(\text{HD}) = 57^\circ$  were reported for these monolayers. The corresponding contact angles on monolayers of octadecanethiol are 112°, 55°, and 47°, respectively.<sup>8</sup>

(26) Shirley, D. A. *Phys. Rev. B* **1972**, *5*, 4709–4714.

(27) Laitinen, H. A.; Chao, M. S. *Anal. Chem.* **1961**, *33*, 1836–1838.

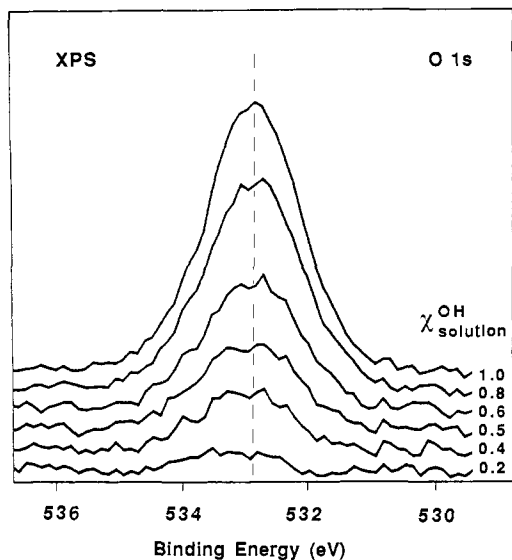


Figure 2. O(1s) peak in the XPS spectrum of monolayers adsorbed from mixtures of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  in ethanol. The data were acquired with a pass energy of 100 eV and a spot size of 1 mm. The spectra are shown after subtraction of the background spectrum acquired on the pure  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  monolayer. The dashed line indicates the peak position for the monolayer of pure  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ .

Typical XPS spectra of the O(1s) region are shown in Figure 2 for mixed monolayers of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ . The spectra are plotted after subtraction of the spectrum obtained from the monolayer of pure undecanethiol. The dashed line shows the position of the peak maximum in the spectrum from the pure hydroxyl-terminated monolayer. A significant shift ( $\sim 0.4$  eV) to higher binding energy occurred as the concentration of hydroxyl groups in the monolayer decreased. This shift is not a consequence of differential charging between samples: the position of the  $\text{Au}(4f_{7/2})$  peak was constant to within  $\pm 0.01$  eV.

We assessed the reliability and accuracy of XPS for quantifying the composition of monolayers by determining the composition of mixed monolayers of  $\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{H}$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  in three different ways (see supplementary material for details). First, the intensity of the O(1s) photoelectrons from each sample was normalized to the intensity of the O(1s) peak from the monolayer adsorbed from a solution containing only  $\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{H}$ . Second, the ratio of the O(1s) intensity to the intensity of the  $\text{Au}(4f_{7/2})$  photoelectrons from the substrate was used as a measure of the relative amount of acid-terminated thiol incorporated in the monolayer. Third, the intensity of the high-energy carbon peak at 289.3 eV arising from  $\text{CO}_2\text{H}$  was used to calculate the composition. The agreement between the three analyses was excellent, indicating that sample-to-sample variations in focus of the spectrometer or the presence of oxygen-containing contaminants does not significantly influence the calculated compositions.

Figure 3 presents the relationship between the composition of the solution<sup>36</sup> in ethanol and the composition of the monolayer for the four systems under study. Only in the mixed Me/Br system did the composition of the monolayer reflect the concentrations

(35) On several occasions, a small oxygen peak (corresponding to  $<5\%$  of the intensity of the peak from a monolayer of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ ) was observed on gold slides that had been immersed in the pure methyl-terminated thiol. In these cases, the area of this residual oxygen peak was subtracted from the areas of all the other samples. The residual oxygen peak was shifted 0.6 eV to lower binding energy from the O(1s) peak arising from the monolayer of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ . Oxygen introduced into the surface of the gold by plasma treatment gives rise to a peak shifted a further 1.5 eV to lower energy; hence, this residual oxygen does not arise from gold oxides. The residual oxygen peak is, however, at a similar energy to the photoelectrons observed from silicones and could arise from trace contamination of the samples by silicone oil.

(36) For clarity, we do not include the solvent in the calculation of the mole fraction in solution. Thus, for two components, A and B,  $\chi_{\text{sol}}^A = [\text{A}]_{\text{sol}} / ([\text{A}]_{\text{sol}} + [\text{B}]_{\text{sol}})$ .

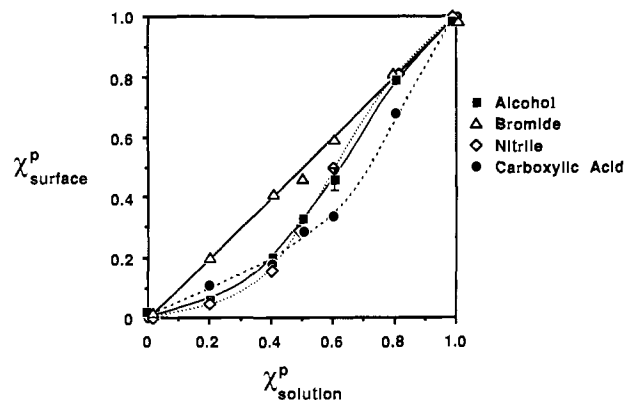


Figure 3. Composition of monolayers adsorbed from ethanolic mixtures of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{H}$  (circles),  $\text{HS}(\text{CH}_2)_8\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_8\text{CN}$  (diamonds),  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{Br}$  (triangles), and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  (squares).  $\chi_{\text{surf}}^p$  represents the mole fraction of the polar-terminated species either in solution or on the surface. The solid and dashed lines are manual fits included simply as a guide to the eye.  $\chi_{\text{surf}}^p$  was calculated from the intensity of the O(1s), N(1s), or Br(3d) photoelectron. The error bar shown is representative of the random errors ( $2\sigma$ ) involved in the analysis of the XPS data.

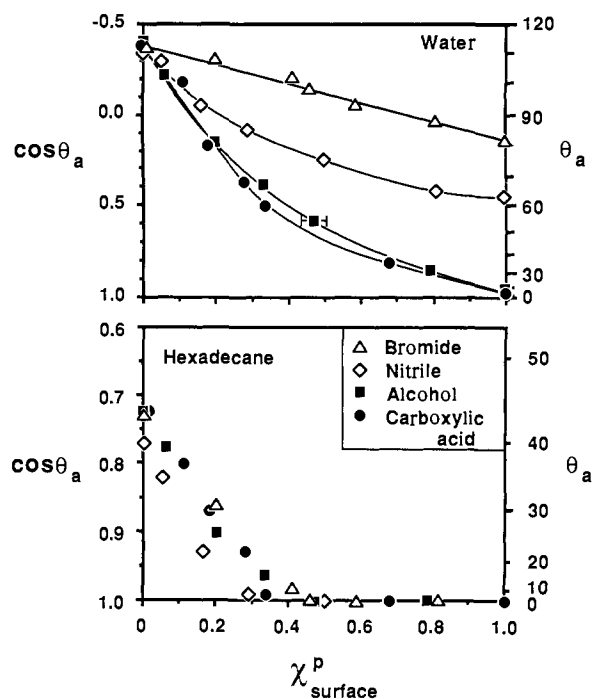
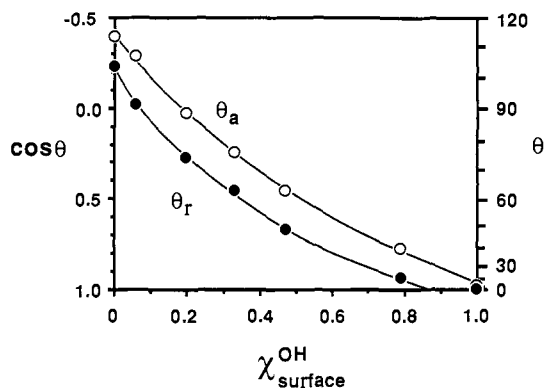


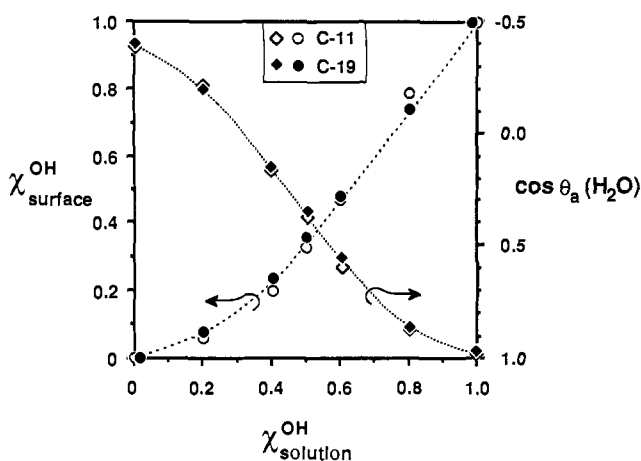
Figure 4. Advancing contact angles of water (upper figure) and hexadecane (lower figure) on monolayers adsorbed from ethanol onto gold slides:  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{H}$  (circles),  $\text{HS}(\text{CH}_2)_8\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_8\text{CN}$  (diamonds),  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{Br}$  (triangles), and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  (squares). Errors in contact angles lie within the symbols. A representative error ( $2\sigma$ ) bar in  $\chi_{\text{surf}}^p$  is shown. The lines in the upper figure are purely to assist the reader.

in solution: the surfaces of the other monolayers were methyl-rich. The advancing contact angles of water and hexadecane are shown in Figure 4 as a function of the mole fraction of the polar component in the monolayer, as determined by XPS. We remeasured the contact angles on the monolayers adsorbed from mixed solutions of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  after immersion of the slides in the adsorption solutions for a further 2 months: the contact angles had not changed significantly.

For the OH/Me system, we also measured the receding contact angles of water. Hysteresis in the contact angle of heterogeneous systems is not well-understood but does give some indication of the distribution of the two adsorbates within the monolayer. If



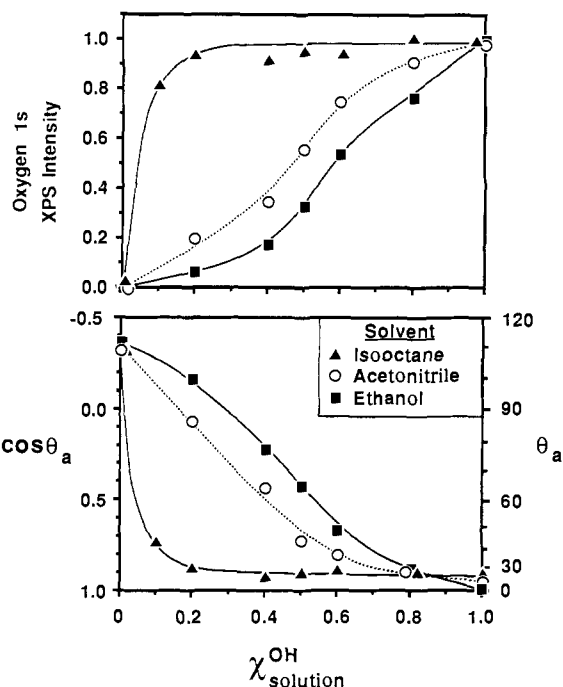
**Figure 5.** Maximum advancing (open circles) and minimum receding contact angles (filled circles) on gold slides after immersion for 2 months in solutions containing mixtures of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ .



**Figure 6.** Comparison of monolayers formed by immersion of gold slides in ethanolic solutions containing mixtures of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  (open symbols) and mixtures of  $\text{HS}(\text{CH}_2)_{18}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{18}\text{CH}_2\text{OH}$  (solid symbols) for 12–24 h: mole fraction of the alcohol-terminated thiol in the monolayer (circles) and advancing contact angles of water (diamonds).

the two components were to segregate into macroscopic domains (vide infra), the nonpolar islands would impede the edge of a drop of water advancing across the surface and the polar islands would likewise pin the edge of a receding drop. Consequently, we would expect the hysteresis to be much greater on the mixed surfaces than on monolayers comprising a single pure component. Figure 5 shows the maximum advancing and minimum receding contact angles of water on OH/Me surfaces. Neither the hysteresis in  $\cos \theta$  nor the hysteresis in  $\theta$  was correlated with the composition or the polarity of the surface. Hysteresis on the mixed surfaces was only slightly greater than on the pure methyl surface. This result agrees with a previous study,<sup>37</sup> which showed that the hysteresis in the contact angles of water pH 3 (so as not to ionize the carboxylic acids) on mixed monolayers of  $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$  and  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$  was independent of the composition of the monolayer in the regime where the receding angle was nonzero.

The chain lengths in these studies were chosen largely on the grounds of solubility and ease of synthesis. Other studies<sup>8,38</sup> have shown that 9- and 11-carbon chains are in a transitional regime between the longer chains, where the properties of the monolayer are largely independent of chain length, and the shorter chains, where the wettability and the structure of the monolayers vary with chain length. It is important to show that the results obtained here are not an artifact of working in this transitional regime but also hold for longer chains. Figure 6 compares the composition of the monolayer and the contact angles obtained for HS-



**Figure 7.** Comparison of monolayers adsorbed onto gold from mixtures of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  dissolved in isooctane (triangles), acetonitrile (circles), and ethanol (squares). Intensity of the O(1s) photoelectron peak normalized to the monolayer adsorbed from a pure solution of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  (upper figure); advancing contact angle of water (lower figure). The solid (ethanol, isooctane) and dotted lines (acetonitrile) are included simply as guides to the eye.

$(\text{CH}_2)_{10}\text{CH}_2\text{OH}/\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  and the 19-carbon analogues  $\text{HS}(\text{CH}_2)_{18}\text{CH}_2\text{OH}/\text{HS}(\text{CH}_2)_{18}\text{CH}_3$ . The two sets of data agree to within experimental error. The advancing contact angles of water published previously<sup>37</sup> for mixed monolayers of  $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$  and  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$  are also in qualitative agreement with the results reported here for  $\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{H}$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ .

**Influence of Solvent on Adsorption.** The nature of the adsorption solvent may influence the composition and structure of a monolayer in several ways. If the components of the monolayer are at, or near, thermodynamic equilibrium with the solution, then a change of solvent will change the activities of the adsorbates in solution and hence change the equilibrium composition of the monolayer. The solvent may be incorporated into the adsorbed monolayer.<sup>39</sup> This problem is likely to be particularly acute if there is geometrical matching between the solvent and the components of the film, e.g., linear, long-chain adsorbates in hexadecane. Finally, if the tail groups are capable of strong, specific interactions, particularly hydrogen bonding, then interactions among the tail groups and between the tail groups and the solvent will control the structure of the monolayer-liquid interface and may affect the structure of the bulk of the monolayer itself.

Gold slides were immersed in solutions containing mixtures of  $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$  and  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$  in a polar, protic solvent (ethanol), a polar, aprotic solvent (acetonitrile), and a nonpolar solvent (isooctane). Figure 7 plots the area of the O(1s) photoelectron peak (normalized to the monolayer adsorbed from a solution of pure 11-hydroxyundecanethiol) and the advancing contact angles of water against the mole fraction of 11-hydroxyundecanethiol in solution. In acetonitrile, the mole fraction of the alcohol in the monolayer varied smoothly with the composition of the solvent but was greater than with ethanol as solvent. The contact angles of water on the monolayers adsorbed from ethanol and acetonitrile fall on the same line when plotted against the composition of the monolayer, with the exception of

(37) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921–937.

(38) Nuzzo, R. G., personal communication.

(39) Levine, O.; Zisman, W. A. *J. Phys. Chem.* **1957**, *61*, 1188–1196. Bewig, K. W.; Zisman, W. A. *J. Phys. Chem.* **1963**, *67*, 130–135. Bartell, L. S.; Betts, J. F. *J. Phys. Chem.* **1960**, *64*, 1075–1076.

Table I. Properties of Monolayers of Thiols Adsorbed onto Gold from Different Solvents

solvent	thiol	XPS peak areas, kcts			$\tau,^a \text{ \AA}$	$\theta_a(\text{H}_2\text{O})^b$	$\theta_a(\text{HD})^c$
		Au(4f <sub>7/2</sub> )	C(1s)	O(1s)			
ethanol	HS(CH <sub>2</sub> ) <sub>10</sub> CH <sub>2</sub> OH	100	87	60	13	<5	
ethanol	HS(CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>	101	87		12	113	44
acetonitrile	HS(CH <sub>2</sub> ) <sub>10</sub> CH <sub>2</sub> OH	98	91	66	17	10	
acetonitrile	HS(CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>	98	90		18	112	44
isooctane	HS(CH <sub>2</sub> ) <sub>10</sub> CH <sub>2</sub> OH	99	95	68	15	29	
isooctane	HS(CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>	105	88		14	110	43
hexadecane	HS(CH <sub>2</sub> ) <sub>10</sub> CH <sub>2</sub> OH	100	93	69	15	24	
hexadecane	HS(CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>	105	86		13	110	43

<sup>a</sup> Ellipsometric thickness. <sup>b</sup> Advancing contact angle of water. <sup>c</sup> Advancing contact angle of hexadecane.

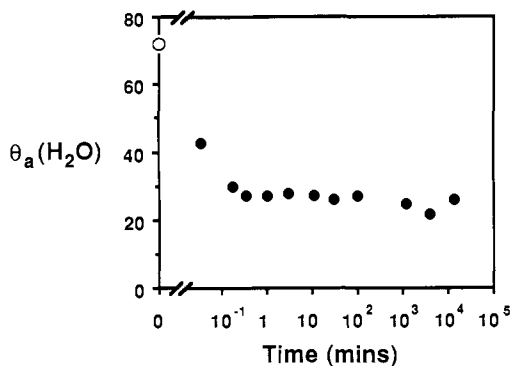


Figure 8. Advancing contact angle of water as a function of the time of immersion of a gold slide in a 1 mM solution in isooctane containing a 4:1 mixture of HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>/HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH. The open circle represents the contact angle of water on the gold slide before immersion in the solution of the thiols. The first data point shown by a filled circle was obtained by dipping the gold slide in the thiol solution and immediately removing the slide and rinsing it with clean ethanol.

the pure monolayer of HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH, which was more hydrophilic when adsorbed from ethanol ( $\theta_a(\text{H}_2\text{O}) < 10^\circ$ ) than acetonitrile ( $\theta_a(\text{H}_2\text{O}) = 19^\circ$ ). In isooctane, monolayers adsorbed from two-component solutions were composed almost exclusively of the hydroxyl-terminated thiol. Only in the most dilute solution (10% HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH, 90% HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>) did the intensity of the O(1s) peak in XPS or the contact angle of water indicate any incorporation of the methyl-terminated species.

The strong preference for adsorption of HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH from isooctane was remarkable. The kinetics of the adsorption process are shown in Figure 8 for a 4:1 mixture of HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>/HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH. The predominance of the hydroxyl-terminated species in the monolayer was established at very short times: the first data point, taken by dipping the slide in the adsorbate solution and immediately rinsing it with clean ethanol, was already characteristic of a fairly polar surface despite the probable kinetic preference for the methyl-terminated thiol during the initial stage of adsorption onto clean gold.<sup>40</sup>

The nature of the solvent not only has a dramatic effect on the composition of the mixed monolayers but also appears to have more subtle effects on the structure of pure monolayers. Table I presents a comparison of monolayers of pure HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH and HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> adsorbed from ethanol, acetonitrile, isooctane, and hexadecane. The differences in thickness, XPS data, and contact angles of water are significant, but the structural implications are unclear.<sup>41</sup> Comparison of the data for monolayers

(40) During the initial stages of formation of the monolayer, the coverage of the surface and the composition of the monolayer are likely to be determined by the sticking coefficient of the thiol on the gold surface and by diffusion of the adsorbates to the gold surface, rather than by interactions between the tail groups of the thiols.

(41) Ulman has obtained a contact angle of 20° for monolayers of hydroxyl-terminated thiols on silver (Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir* 1989, 5, 101-111). The hydrocarbon chains in monolayers on silver are less canted than on gold (~0° versus 30°), resulting in a different orientation of the hydroxyl groups at the interface with the supernatant water. Clearly, the structure, and not merely the number density, of the hydroxyl groups at the monolayer-liquid or monolayer-vapor interface is important in determining wettability.

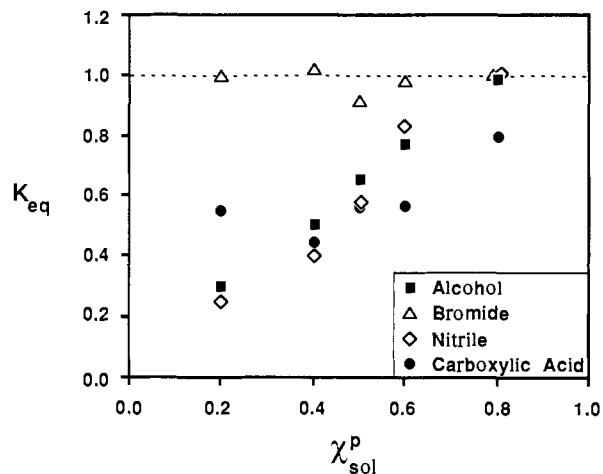


Figure 9.  $K_{eq}$  (see text for definition) plotted as a function of the mole fraction of the polar-terminated species in solution for the adsorption of monolayers from solutions in ethanol: HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> and HS(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H (circles), HS(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub> and HS(CH<sub>2</sub>)<sub>8</sub>CN (diamonds), HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> and HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>Br (triangles), and HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> and HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH (squares). The errors in the values of  $K_{eq}$  may be quite large at  $\chi_{sol}^p = 0.2$  and 0.8, perhaps  $\pm 0.1$ .

adsorbed from hexadecane (a linear, rodlike molecule) and isooctane (a small, globular molecule) shows no indication of the trapping of solvent in these monolayers.

## Discussion

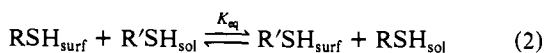
Several species other than thiols, including disulfides (RSSR), sulfides (RSR), and phosphines (R<sub>3</sub>P), adsorb from solution and form stable monolayers on gold.<sup>42</sup> None of the other film-forming molecules surveyed formed a monolayer whose quality was clearly superior to that of a monolayer formed from a thiol and most, as indicated by contact angles, formed inferior monolayers. Dialkyl sulfides and substituted thiophenes offer greater electrochemical stability than thiols and, together with disulfides, allow one to introduce equal concentrations of two functional groups into the monolayer by using dissimilar chains. We have shown, however, that polyfunctional surfaces can also be constructed by competitive adsorption of thiols, with full control over the relative concentrations of the different components in the monolayer. Adsorption of thiols appears to be strongly favored over disulfides or sulfides from multicomponent solutions. Consequently, control over the structure of the monolayer is most easily obtained if the same head group is employed for each component, with changes introduced only in the chains and tail groups. The strong adsorption of thiols compared to the other tail groups in this study makes binding of both the head and tail groups to the gold surface unlikely. No evidence for such looping has been observed, except in the case of  $\alpha,\omega$ -dithiols.<sup>8</sup>

The composition of a monolayer adsorbed from a solution containing two thiols is not, in general, determined by a simple equilibrium expression. If the monolayer and the solution are

(42) Some other functional groups, such as selenides, which were not studied here, may also form monolayers on gold.



in equilibrium, then we can define  $K_{\text{eq}}$  by eq 3. If the monolayer



$$K_{\text{eq}} = \frac{[\text{RSH}]_{\text{sol}}[\text{R}'\text{SH}]_{\text{surf}}}{[\text{RSH}]_{\text{surf}}[\text{R}'\text{SH}]_{\text{sol}}} \quad (3)$$

were to act as an ideal two-dimensional solution,<sup>43</sup> then  $K_{\text{eq}}$  would be constant with a value that reflected the relative solubilities of the two thiols (since, to a very rough approximation, the environment of the adsorbates in a pure monolayer is similar to that in a crystal of that component). Figure 9 plots  $K_{\text{eq}}$ , calculated by using eq 3 and the data from Figure 3, against the mole fraction of the polar species in solution in ethanol. Only in the Br/Me system were the composition of the solution and the monolayer the same. Neither the Br nor the CH<sub>3</sub> tail group has a strong specific interaction with the solvent.<sup>44</sup> Since there was no apparent preference for adsorption of either species, we may infer an absence of strong specific interactions within the monolayer. For the CO<sub>2</sub>H/Me system, adsorption of the methyl-terminated species was preferred at all concentrations, reflecting better solvation of the carboxylic acids in solution in ethanol than at the surface of the monolayer.<sup>45</sup>

The OH/Me and CN/Me systems are the most interesting. In both these systems, adsorption of the component with the polar tail group was strongly disfavored at low concentrations in solution, but  $K_{\text{eq}}$  approached unity as  $\chi^{\text{p}}$  approached one. This behavior is similar to that observed in regular solutions with an excess free energy of mixing  $G^{\text{excess}} = \xi\chi^{\text{p}}\chi^{\text{np}}$ , where  $\xi$  is a positive constant.<sup>46</sup> In solutions of *n*-alkanes and *n*-alcohols, breaking of hydrogen bonds leads to large positive excess enthalpies of mixing.<sup>47</sup> A similar effect in the monolayer could account for the adsorption isotherm obtained for the OH/Me system. Careful study of Figure 2 reveals that, at low concentrations of OH in the surface, the O(1s) photoelectron peak shifted to higher energy by about 0.4 eV. This shift in the peak position implies that the hydroxyl groups are in different environments at low  $\chi^{\text{p}}_{\text{surf}}$  and high  $\chi^{\text{p}}_{\text{surf}}$ . A possible explanation is that, at low  $\chi^{\text{p}}_{\text{surf}}$ , the OH groups in the monolayer are isolated and can only form hydrogen bonds to the solvent. At higher concentrations, the OH groups start to aggregate and form H bonds within the monolayer as well as with the solvent. These interactions would favor monolayers comprising either the pure methyl-terminated species or the pure hydroxyl-terminated species but disfavor monolayers containing a mixture of the two components.<sup>48</sup>

One can postulate a similar rationalization for the data for CN/Me. Poorer solvation of the dipolar nitrile group in the monolayer than in solution would disfavor adsorption of HS-(CH<sub>2</sub>)<sub>8</sub>CN. As the concentration of nitrile groups in the monolayer increased, a favorable dipole-dipole interaction could stabilize the nitrile groups at the interface and lead to an increase in  $K_{\text{eq}}$ .<sup>49</sup>

An unknown factor in these studies is the effect of the structure of the solvent at the monolayer-ethanol interface. As the surface

of the monolayer changes from hydrophilic to hydrophobic, the solvent molecules almost certainly reorient to place their methyl groups rather than their alcohol groups adjacent to the monolayer.<sup>50</sup> As a consequence, solvation of polar groups embedded in a largely nonpolar interface might be poor.

*The wettability of mixed monolayers is nonideal.* If the two components of a monolayer were to act independently, then the contact angles would follow Cassie's law,<sup>20</sup>

$$\cos \theta = \chi_1 \cos \theta_1 + \chi_2 \cos \theta_2 \quad (4)$$

where  $\chi_1$  and  $\chi_2$  are the mole fractions of the two components in the monolayer and  $\theta_1$  and  $\theta_2$  are the contact angles on pure monolayers of the two components. Consequently, a graph of  $\cos \theta$  against  $\chi^{\text{p}}_{\text{surf}}$  would be linear (Figure 4). For water on mixed Br/Me surfaces, and for hexadecane on all the surfaces, the intermolecular forces between the monolayer and the probe liquid are largely dispersive and Cassie's Law appears to hold reasonably well (at least over the limited range in which  $\theta_a(\text{HD})$  is nonzero).<sup>51</sup>

The contact angles of water on surfaces containing alcohol, carboxylic acid, or nitrile groups, in which specific H-bonding interactions are important, deviate strongly from linearity. The apparent hydrophilicity of the polar tail groups is higher when they are in a nonpolar environment composed largely of methyl groups than when their neighbors are other polar groups. Two plausible explanations for these deviations are poor electrostatic solvation of the polar tail groups at low  $\chi^{\text{p}}$  in the low dielectric constant medium provided by the surrounding methyl groups and poor hydrogen-bonding between dilute protic tail groups in the monolayer. The latter explanation is certainly consistent with the XPS data for the O(1s) photoelectrons and with the form of the adsorption isotherms.

*Two-component monolayers do not phase-segregate into macroscopic islands.* Alcohols and carboxylic acids self-associate in alkane solvents, so it is likely that association also occurs in the quasi-two-dimensional solution represented by the monolayer. There are several pieces of evidence, however, that suggest that macroscopic islands do not form.

First, if a monolayer is in equilibrium with a large excess of adsorbate in solution, the chemical potential of the components in solution is independent of the composition of the monolayer. The chemical potential of a molecule in a macroscopic, single-component domain is also essentially independent of the composition of the monolayer. The free energy of formation of a monolayer composed of macroscopic islands would thus be a linear function of the composition of the monolayer. Consequently, macroscopic, single-component domains would be disfavored thermodynamically with respect to a pure monolayer of the component for which  $\mu_{\text{sol}} - \mu_{\text{surf}}$  is greatest. Islands could form if the composition of the monolayer were kinetically frozen at some nonequilibrium value, with subsequent lateral diffusion resulting in the formation of single-component domains. Although lateral diffusion in the monolayer is a priori plausible,<sup>52</sup> evidence such as the preferential adsorption of HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH from solutions

(43) The solutions were sufficiently dilute that they may be treated as ideal dilute solutions.

(44) Alkanes interact by dispersive forces; bromoalkanes interact largely by dispersive forces with only a small polar interaction.

(45) Since the polarizabilities of ethanol and hydrocarbons are similar, differences in the solvation of the methyl group between the solution and the monolayer are probably small.

(46) The term "regular solution" was coined by Hildebrand to refer to solutions with an ideal entropy of mixing but a nonzero enthalpy of mixing (Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold: New York, 1970). The definition we use here is that given by Rowlinson (Rowlinson, J. S. *Liquids and Liquid Mixtures*; Butterworth: London, 1969). Though useful as a model, the monolayers are almost certainly not strictly regular.

(47) Costas, M.; Patterson, D. J. *Thermochim. Acta* **1987**, *120*, 161-181.

(48) The mixed monolayers composed of methyl-terminated and carboxylic acid terminated thiols did not exhibit a very low value of  $K_{\text{eq}}$  at low  $\chi^{\text{p}}$ , possibly because the carboxylic acids are dimerized even at low concentrations in the monolayer.

(49) The dipole-dipole interaction can be either positive or negative. A favorable interaction implies that the CN moieties in the monolayer are canted at least 35° from the normal to the surface.

(50) The surface tension of ethanol is almost purely dispersive and is comparable in magnitude to alkanes, which suggests that the methyl groups of the ethanol molecule are oriented outward at the ethanol-air interface (Harkins, W. D.; Davis, E. C. H.; Clark, G. L. *J. Am. Chem. Soc.* **1917**, *39*, 541-596). The same orientation is likely at an ethanol-hydrocarbon interface.

(51) For Cassie's law to hold, the solid-liquid free energy  $\gamma_{\text{sl}} = \chi_1\gamma_{\text{sl},1} + \chi_2\gamma_{\text{sl},2}$ , where  $\gamma_{\text{sl},i}$  is the solid-liquid free energy between a pure monolayer of component *i* and a liquid. Fowkes (Fowkes, F. M. *Ind. Eng. Chem.* **1964**, *56*(12), 40-52) proposed that, for purely dispersive interactions at the interfaces, the geometric mean approximation can be applied to  $\gamma_{\text{sl}}$ . For water on a dispersive solid, Fowkes' approach yields  $\gamma_{\text{sl}} = \chi_1\gamma_{\text{sv},1} + \chi_2\gamma_{\text{sv},2} + \gamma_{\text{lv}} - 2[(\gamma_{\text{lv}}(\chi_1\gamma_{\text{sv},1} + \chi_2\gamma_{\text{sv},2}))^{1/2}]$ , where  $\gamma_{\text{lv}}$  is the dispersive part of the liquid surface free energy. By substituting this expression in Young's equation, we obtain  $\cos \theta$  as a function of the surface composition. The geometric mean approximation predicts that  $\cos \theta$  should be convex as a function of  $\chi^{\text{p}}$ , not linear as predicted by Cassie. The difference between the two predictions for the Br/Me system is small—less than 3°—so we cannot make a clear distinction between the two approaches based on our data.

(52) Although lateral diffusion on the surface may be facile in the liquidlike monolayers that exist during the adsorption of the monolayers, in the pseudocrystalline state of the fully formed monolayers lateral motion is likely to be much slower, akin to diffusion in organic solids or liquid crystals.



in isoctane containing much higher concentrations of HS-(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> (Figure 8) militates against kinetic control over the initial composition of the monolayer.

Second, the contact angles of water on the mixed monolayers do not show the behavior expected of a monolayer composed of discrete islands large enough to influence the contact angle. Nonpolar islands composed of methyl groups would pin the advancing contact angle and cause the plots of  $\cos \theta$  against  $\chi^p_{\text{surf}}$  to be convex rather than concave. Polar islands would pin the receding contact angles and be reflected in greatly increased hysteresis in mixed monolayers, contrary to the relatively constant hysteresis observed on the mixed OH/Me surfaces. It has been estimated theoretically<sup>53</sup> that islands would have to be greater than about 0.1  $\mu\text{m}$  in size to cause observable hysteresis, thus placing an upper bound on the size of any domains, although this limit has not been established experimentally.

Third, a thin film of water condenses onto a pure carboxylic acid surface at 100% relative humidity (RH). Consequently, at 100% RH, hexadecane beads on pure monolayers of carboxylic acid terminated thiols or methyl-terminated thiols ( $\theta_a(\text{HD}) = 35\text{--}40^\circ$ ,  $47^\circ$  respectively). If the mixed monolayers were to comprise discrete islands, each of which was oleophobic, then the monolayer itself would not be wetted by hexadecane. We observed that hexadecane spread on mixed CO<sub>2</sub>H/Me monolayers with  $\chi^p > 0.4$  at all humidities.

Other evidence suggests that any clusters of one component must be sufficiently small that the molecules in the cluster are still influenced by the other component in the monolayer. First, the nonideal behavior of the composition and contact angles of the monolayers requires that the energetics of the monolayer vary with composition and hence that the two components in the monolayer interact. Second, the O(1s) peak of the hydroxyl terminus in the XPS spectra of mixed OH/Me monolayers shifted to higher energies as the mole fraction of the alcohol in the surface decreased. XPS provides a probe of the local structure in the monolayer. Changes in the shape and position of the O(1s) peak probably arise from interactions with the nearest-neighbor molecules in the monolayer and suggest that at low  $\chi^p_{\text{surf}}$  aggregates of alcohol groups comprise at most a few molecules. Third, in another study published separately, we have titrated<sup>54</sup> the carboxylic acids in mixed CO<sub>2</sub>H/Me surfaces. The onset of ionization moved to higher pH as the mole fraction of the acid in the monolayer decreased, suggesting changes in the local environment with composition.

For many studies of mixed monolayers, 16 carbons seems to be the optimal chain length.<sup>11,37,55</sup> The 11-carbon chains, used primarily in these studies, have some advantages over longer chains. Long-chain molecules, particularly those with more than 20 carbons, become progressively harder to synthesize and purify. Short chains are also more soluble than long chains and allow a wider range of concentration and choice of solvents. Monolayers formed from 11-carbon chains reach equilibrium, or at least a metastable composition, after immersion overnight in the adsorption solutions: the contact angles of water on the mixed monolayers of HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH and HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> adsorbed from ethanol did not change upon immersion for an additional 10 weeks, and the monolayers adsorbed from acetonitrile were unchanged 4 months later. On the other hand, the composition of several of the monolayers adsorbed from mixtures of long- and short-chain thiols (see companion paper) evolved slowly for several weeks after immersion. The drawback of 11-carbon chains is that they are close to the chain length at which the structure and properties of the monolayers of short thiols differ from monolayers of longer thiols. Thiols with hydrocarbon chains of 16 carbons

(for which synthetic precursors are commercially available) have many of the characteristics that are favorable in both shorter and longer chains.

The assumption of thermodynamic equilibrium allows us to rationalize the relationships between the concentrations in solution and the compositions of mixed monolayers of thiols on gold. In ethanol, undecanethiol was adsorbed preferentially from mixtures of HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH and HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> at all compositions, but particularly at low  $\chi^p_{\text{sol}}$ . In acetonitrile, whichever component was more concentrated was adsorbed preferentially. In isoctane, HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH was adsorbed to the almost total exclusion of HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>, even when HS(CH<sub>2</sub>)<sub>10</sub>CH<sub>2</sub>OH was the minor component in solution. This variation in composition with solvent strongly suggests thermodynamic rather than kinetic control over the composition of the monolayer. It is difficult to conceive of a kinetic rationale for the widely different rates of adsorption that would be required for kinetically controlled compositions. It is well-known that alcohols associate in alkane solutions, largely to form tetramers, but at the low concentrations employed here, the monomer predominates.<sup>56</sup> Consequently, the diffusion rates of the two components to the surface should be comparable in an alkane solvent. Furthermore, both tail groups are of similar size and neither is strongly solvated in the alkane solution, so there are no obvious steric grounds for disfavoring one component. The composition of the monolayers can be rationalized qualitatively on thermodynamic grounds by considering the changes in activity of the solutes in different solvents. Long-chain alkanethiols are more soluble in alkane solvents than in ethanol, whereas the converse is true for 11-hydroxyundecanethiol. If one assumes that the activities of the two components in the monolayer are, to first order, independent of the solvent, then, as the solvent is made progressively less polar, more of the alcohol-terminated species should be incorporated into the monolayer.

If the adsorption process were under kinetic control, any preference for one thiol would be approximately independent of the concentrations of the two thiols in solution. The large variations in  $K_{\text{eq}}$  with composition for three of the systems studied are inconsistent with a simple kinetic model but can be rationalized, within a thermodynamic model, by consideration of intramonolayer interactions.

We are still faced with the problem that equilibration in fully formed monolayers (Figure 1) is clearly not sufficiently rapid to account for the compositions observed after very short immersion times (Figure 8). Although we have not yet proven a mechanism by which the components in the monolayer and the precursors in solution equilibrate, the assumption that the compositions of the monolayers are at, or near, their values at thermodynamic equilibrium with the solution provides a framework for interpreting the structure and properties of the mixed monolayers.

## Conclusions

Long-chain alkanethiols form ordered, oriented monolayers on gold and are adsorbed preferentially over molecules containing a wide range of other functional groups. None of the other functionalities studied led to monolayers on gold that were clearly superior in quality to those obtained from thiols. Other sulfur-containing species such as disulfides, sulfides, and xanthates also formed monolayers. The only head group that did not contain sulfur and that could be used to form monolayers with contact angles comparable to monolayers of alkanethiols was a trialkylphosphine, R<sub>3</sub>P.

Monolayers exposing more than one functional group at their surfaces can be synthesized by coadsorbing thiols with different tail groups from solution. In this paper, we have studied exclusively monolayers containing two components, one of which was terminated by a methyl group. These simple systems are easier to analyze and interpret than more complex monolayers containing additional components or two strongly interacting tail groups. The principles here are generalizable to more complex systems. We

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make six key observations regarding mixed monolayers:

(1) Multicomponent monolayers do not segregate into discrete single-component domains. Any islands that do form are too small to influence the contact angle by distorting the drop edge, placing an upper bound of about  $0.1 \mu\text{m}$  on the size of any such islands. The adsorption isotherms and the variation in contact angle with composition and relative humidity suggest further that any single-component domains can be no more than a few tens of angstroms across. Changes in acidity and in the energies of X-ray photoelectrons suggest local structural variations on a molecular scale. We have no evidence for two-dimensional order in the tail groups, but the distribution of tail groups is unlikely to be entirely random. The nonideality of the adsorption isotherms suggests cooperativity between components in the monolayer that would lead to some degree of aggregation.

(2) The composition and structure of monolayers adsorbed from solutions containing mixtures of thiols are consistent with thermodynamic control over the composition of the monolayer. The composition of the monolayer can be predicted qualitatively by considering the activities of the components in the monolayer and in solution and specific interactions between the components in the monolayer. It is difficult to construct a kinetic model that rationalizes the adsorption isotherms in this and the following paper in this issue. The mechanism by which equilibration between the monolayer and the solution occurs is, however, still unclear.

(3) Mixed monolayers do not act as ideal two-dimensional solutions. In particular, tail groups that form strong hydrogen bonds are disfavored in the nonpolar environment provided by surfaces composed largely of methyl groups. As the proportion of polar groups in the monolayer increases, interactions between tail groups appear to stabilize the polar groups at the interface. In principle, interactions between polar groups could also be unfavorable but were favorable in the three systems studied here.

(4) The two components of the monolayer do not act independently in determining the wettability of the surface. Polar

groups are more hydrophilic when they are in the nonpolar environment provided by methyl groups than when the surface of the monolayer is composed largely of other polar groups.

(5) The hysteresis in the contact angle of water on monolayers derived from thiols is small and is approximately independent of the polarity of the tail groups. In mixed monolayers containing a polar and a nonpolar component of the same chain length, the hysteresis is independent of the composition of the monolayer.

(6) The nature of the adsorption solvent has a dramatic effect on the composition of the monolayers, probably largely through changes in the activity of the solutes. We have no evidence for incorporation of solvent in the monolayers studied here.

**Acknowledgment.** We are grateful to R. Nuzzo (AT&T Bell Laboratories), to J. Hickman (M.I.T.), and to our colleagues E. B. Troughton, P. Laibinis, and H. Biebuyck, who have worked on related systems, for valuable discussions. We thank Prof. A. L. Smith (Unilever) for pointing out the parallels with the behavior of regular solutions.

**Registry No.** Au, 7440-57-5;  $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$ , 544-76-3;  $\text{HS}(\text{C}-\text{H}_2)_{10}\text{CH}_2\text{OH}$ , 73768-94-2;  $[\text{S}(\text{CH}_2)_{10}\text{CH}_2\text{OH}]_2$ , 119438-02-7;  $[\text{S}(\text{C}-\text{H}_2)_{10}\text{CH}_3]_2$ , 79458-27-8;  $\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{H}$ , 71310-21-9;  $\text{HS}(\text{CH}_2)_{10}\text{C}-\text{H}_2\text{Br}$ , 116129-34-1;  $\text{HS}(\text{CH}_2)_8\text{CN}$ , 117559-63-4;  $\text{HS}(\text{CH}_2)_8\text{CH}_3$ , 1455-21-6;  $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ , 5332-52-5;  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ , 112-55-0;  $\text{HS}(\text{C}-\text{H}_2)_{15}\text{CH}_3$ , 2917-26-2;  $\text{HS}(\text{CH}_2)_{18}\text{CH}_3$ , 53193-23-0;  $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ , 7773-83-3;  $\text{HS}(\text{CH}_2)_{18}\text{CH}_2\text{OH}$ , 114896-31-0;  $\text{Br}(\text{CH}_2)_{18}\text{CH}_2\text{OH}$ , 121497-31-2; 1,8-dibromooctane, 4549-32-0; 11-undecenylmagnesium bromide, 88476-93-1; 19-bromo-1-nonadecene, 121497-30-1; disiamylborane, 1069-54-1.

**Supplementary Material Available:** Details of the synthesis of  $\text{HS}(\text{CH}_2)_{19}\text{OH}$ , the competitive adsorption of thiols with phosphines, isonitriles, and disulfides, and the measurement of surface compositions by XPS (7 pages). Ordering information is given on any current masthead page.

## Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Length of the Alkyl Chain<sup>1</sup>

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**Abstract:** Mixtures of two long-chain alkanethiols,  $\text{HS}(\text{CH}_2)_n\text{X}$  and  $\text{HS}(\text{CH}_2)_m\text{Y}$  ( $\text{X}, \text{Y} = \text{CH}_3, \text{OH}; n > m$ ), in which the alkyl chains have different lengths, adsorb from solution onto gold and form monolayers comprising a densely packed inner region adjacent to the gold surface and a disordered outer region in contact with the solution. When  $\text{X} = \text{Y} = \text{CH}_3$  ( $n \neq m$ ), this disordered phase makes the "mixed monolayer" more oleophilic than the ordered, pure (i.e., single-component) monolayers. When  $\text{X} = \text{Y} = \text{OH}$ , the pure monolayers are wetted by water, but the mixed monolayers are less hydrophilic because nonpolar polymethylene chains are exposed at the surface. When  $\text{X} = \text{CH}_3, \text{Y} = \text{OH}$  ( $n = 21, m = 11$ ), a very sharp transition occurs from a monolayer composed largely of the longer, methyl-terminated component to the shorter, hydroxyl-terminated component as the mole fraction of  $\text{HS}(\text{CH}_2)_{11}\text{OH}$  in the adsorption solution is increased. From solutions containing two thiols, adsorption of the thiol with the longer chain is preferred. This preference is greater when the monolayers are adsorbed from ethanol than from isooctane. The mixed monolayers do not act as ideal two-dimensional solutions. The adsorption isotherms suggest a positive excess free energy of mixing of the two components in the monolayer. The compositions of the monolayers appear to be determined largely by thermodynamics, although in some cases there is also a kinetic contribution. The two components in the mixed monolayers do not phase-segregate into macroscopic islands (greater than a few tens of angstroms across) but are probably not randomly dispersed within the monolayer. The wettability of mixed, methyl-terminated monolayers can be partially rationalized by the geometric mean approximation, but a full description probably requires inclusion of the entropy of mixing at the monolayer-liquid interface. The hysteresis in the contact angle on these monolayers cannot be explained by theories of wetting based on macroscopic heterogeneity. Contact angles are more sensitive than optical ellipsometry or X-ray photoelectron spectroscopy to certain types of changes in the composition and structure of these monolayers.

Long-chain alkanethiols,  $\text{HS}(\text{CH}_2)_n\text{X}$ , adsorb from solution onto gold and form densely packed monolayer films.<sup>3-5</sup> This paper

is the second of two that present studies of the "mixed monolayers" formed by the coadsorption of two thiols. In the preceding paper