Comparison of Self-Assembled Monolayers on Gold: Coadsorption of Thiols and Disulfides[1]

Colin D. Bain,[2] Hans A. Biebuyck, and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

Received October 4, 1988. In Final Form: January 4, 1989

Ordered, organic monolayers were formed on gold slides by adsorption from ethanol of $HS(CH_2)_{10}CH_2OH$, $HS(CH_2)_{10}CH_3$, $[S(CH_2)_{10}CH_2OH]_2$, $[S(CH_2)_{10}CH_3]_2$, and binary mixtures of these molecules in which one component was terminated by a hydrophobic methyl group and one by a hydrophilic alcohol group. The compositions of the monolayers were determined by X-ray photoelectron spectroscopy (XPS). Wettability was used as a probe of the chemical composition and structure of the surface of the monolayer. When monolayers were formed in solutions containing mixtures of a thiol and a disulfide, adsorption of the thiol was strongly preferred ($\sim$75:1). The advancing contact angles of water and hexadecane on monolayers formed from solutions containing mixtures of two thiols, a thiol and a disulfide, or two disulfides were dependent on the proportion of hydroxyl-terminated chains in the monolayer and largely independent of the nature of the precursor species. This observation suggests that both thiols and disulfides give rise to the same chemical species (probably a thiolate) on the surface. This model is supported by the observation by XPS of indistinguishable S(2p) signals from monolayers derived from thiols and disulfides.

Introduction

Both long-chain alkanethiols and dialkyl disulfides adsorb from solution onto gold and form ordered, oriented monolayers.[3-6] These self-assembled monolayers have been used in examining electrochemical processes,[7] in promoting adhesion,[8] in studying wettability,[9] and in

(1) Supported in part by the Office of Naval Research and the Defense Advanced Research Projects Agency. The XPS spectrometer was purchased through a DARPA/URI and is housed in the Harvard University Materials Research Laboratory, an NSF-funded facility.

(2) IBM Pre-Doctoral Fellow in Chemistry, 1985-86.

(3) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481-4483.

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

(5) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559-3568.

(6) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321-335.

(7) Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107-6108. Finklea, H. O.; Avery, S.; Lynch, M.; Furtsch, T. *Langmuir* **1987**, *3*, 409-413. Rubenstein, I.; Steinberg, S.; Tor, Y.; Shanzer, A.; Sagiv, J. *Nature* **1988**, *332*, 426-429. Sabatani, E.; Rubenstein, I.; Maoz, R.; Sagiv, J. *J. Electroanal. Chem.* **1987**, *219*, 365-371. Taniguchi, I.; Toyosawa, K.; Yamaguchi, H.; Yasukouchi, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1032-1033.

modeling complex interfaces of membranes and polymers.[10] In constructing a monolayer with specific properties, the choice between thiols and disulfides is governed by many considerations, including solubility, reactivity, stability, and ease of synthesis of the adsorbate. The structure and properties of the monolayers formed from thiols and disulfides have, however, not been directly compared. This paper is the first of two that compare self-assembled monolayers of thiols and disulfides.

Previous studies by Dubois et al.[11] of the adsorption of dimethyl disulfide and methanethiol on gold in UHV indicated large differences in the energy of adsorption of the two species. Dimethyl disulfide formed a strongly bound, chemisorbed state with an activation energy of desorption of 28 kcal/mol of disulfide, but the methanethiol was only physisorbed on the gold surface and desorbed intact at -45 °C. When adsorbed from solution onto gold, alkanethiols reach a strongly chemisorbed state, which was inaccessible in the UHV experiment. The difference between experiments in UHV and solution is not entirely clear. Dubois et al.[11] have proposed that the chemisorbed species formed from the disulfide on gold in UHV is a thiolate, RS^-. We believe that the species ultimately formed on the surface by adsorption of thiols or disulfides from solution is also a thiolate, but the mechanism for the conversion of the thiol to the thiolate is not yet known. Conversion of the physisorbed thiol to the chemisorbed thiol may not occur in UHV either because the activation barrier to chemisorption of the thiol from the initial, physisorbed state is higher than the barrier to desorption or possibly because the presence of air or another oxidant is required for this conversion to occur. Strong and Whitesides[12] have shown by TEM that monolayers of docosanethiol and didocosyl disulfide, adsorbed from solution, have the same lateral order on the (111) face of gold but the disulfide shows additional phases on the (100) face. In a previous paper we demonstrated qualitatively that thiols are adsorbed preferentially onto gold from solutions containing mixtures of thiols and disulfides.[6,13]

In this paper we compare monolayers formed from mixtures of undecanethiol ($HS(CH_2)_{10}CH_3$) and 11-hydroxyundecanethiol ($HS(CH_2)_{10}CH_2OH$), from the analogous disulfides, and from mixtures of these thiols and disulfides. In each case, one of the adsorbates exposed a hydrophobic methyl group at the surface and the other a hydrophilic hydroxyl group. We seek to answer two principal questions. First, how great is the preference for adsorption of thiols from binary mixtures of thiols and disulfides in solution, and is this preference kinetic or thermodynamic? Second, do the wetting properties of the monolayers depend on the origin of the components of the monolayer? We find that, despite a ~75:1 preference for adsorption of thiols over disulfides, the wettability of the resulting monolayers is largely independent of the origin of the monolayer components.

A subsequent paper will present a more extensive comparison of monolayers of thiols and disulfides and will include a discussion of the dynamics of adsorption and the effects on the monolayers of varying the solvent and the conditions of adsorption. The paper will also address in more detail the subtle differences that exist between fully formed monolayers of pure thiols and disulfides.

We chose methyl- and hydroxyl-terminated species for this study so that the wettability of the monolayers would be sensitive to their composition and so that the composition of the monolayer could be determined by X-ray photoelectron spectroscopy (XPS). Since the methyl group is nonpolar and hydrophobic and the alcohol is polar and hydrophilic, contact angles were a sensitive probe of the structure of the surface. The oxygen of the alcohol group provided the handle for determining the composition of the monolayers by XPS.

Three experiments constituted this study, each comprising the analysis of a set of monolayers adsorbed from solutions containing different mole fractions of a methyl-terminated and a hydroxyl-terminated adsorbate: $HS(CH_2)_{10}CH_2OH$ and $[S(CH_2)_{10}CH_3]_2$, $HS(CH_2)_{10}CH_3$ and $[S(CH_2)_{10}CH_2OH]_2$, and $[S(CH_2)_{10}CH_3]_2$ and $[S(CH_2)_{10}CH_2OH]_2$. We also compared the wettability of these monolayers with those formed from mixtures of $HS(CH_2)_{10}CH_2OH$ and $HS(CH_2)_{10}CH_3$[14] and with a monolayer formed from the mixed disulfide $HO(CH_2)_{11}SS(CH_2)_{10}CH_3$.

Experimental Section

Materials. The gold substrates for these experiments were prepared by either thermal or electron-beam evaporation of 1000–2000 Å of gold onto 3-in. silicon(111) wafers precoated with 50 Å of chromium or sputtered with argon to improve adhesion. These procedures produce polycrystalline films with a strong (111) texture.[4,15] The wafers were stored in polypropylene containers (Fluoroware) until use, which was generally within 1 day of evaporation. Ethanol (US Industrials Co.) was deoxygenated with bubbling nitrogen. Hexadecane (Aldrich, 99%) was percolated twice through neutral, grade 1 alumina, after which it passed the Bigelow test.[16] Water was deionized and then distilled in a glass and Teflon still. Undecanethiol, docosanethiol, diundecyl disulfide, 11-hydroxyundecanethiol, and bis(11-hydroxyundecyl) disulfide were available from previous studies.[6] A sample of gold(I) hexadecyl thiolate was kindly provided by G. Ferguson. Dioctyl disulfide (Fairfield Research Chemicals) was distilled (0.15 Torr, 118 °C) and chromatographed (50:1 hexane/ethyl acetate, Silica Gel 60 (Merck)) before use: it gave a negative test with Ellman's reagent,[17] indicating an absence of thiol impurities (<0.1% thiol).

11-Hydroxyundecyl Undecyl Disulfide. A solution of undecanethiol (0.5 g, 2.6 mmol, chromatographed with 50:1 hexane/ethyl acetate on Silica Gel 60 (Merck, 9 × 3/4 in. column)) and 11-mercapto-1-undecanol (0.54 g, 2.6 mmol) in 20 mL of anhydrous ethanol was warmed to 40 °C and titrated to a yellow-brown end point with a 10 mM solution of iodine in ethanol. The ethanol was removed on a rotary evaporator, and the resulting yellow solid was dissolved in 20 mL of ether, washed with distilled water (3 × 10 mL), and dried over anhydrous $MgSO_4$. Evaporation of the solvent yielded a white solid that gave a negative test with Ellman's reagent, indicating the absence of thiols as impurities. The mixture of disulfides was separated chromatographically (3:1 hexane/ethyl acetate; 9 × 3/4 in. column, Silica Gel 60 (Merck)) to yield 0.41 g (1.1 mmol, 42%) of 11-hydroxyundecyl undecyl disulfide as a white solid: mp 57.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.61 (q, 2 H), 2.65 (t, 4 H), 1.73 (m, 4 H), 1.55 (m, 2 H), 1.2–1.4 (m, 30 H), 0.85 (t, 3 H).

Anal. Calcd (Found) for $C_{22}H_{46}OS_2$: C, 67.63 (67.46); H, 11.87 (11.85).

(8) Stewart, K. R.; Whitesides, G. M.; Godfried, H. P.; Silvera, I. F. *Rev. Sci. Instrum.* **1986,** *57,* 1381–1383.

(9) Bain, C. D.; Whitesides, G. M. *Science* **1988,** *240,* 62–63. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988,** *110,* 3665–3666. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988,** *110,* 5897–5898.

(10) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988,** *4,* 921–937. Diem, T.; Czajka, B.; Weber, B.; Regen, S. L. *J. Am. Chem. Soc.* **1986,** *108,* 6094–6095.

(11) Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987,** *109,* 733–740.

(12) Strong, L.; Whitesides, G. M. *Langmuir* **1988,** *4,* 546–558.

(13) The purpose of the earlier study was merely to demonstrate that trace contamination of thiols by disulfides (formed by air oxidation of the thiol) is not a serious problem in the formation of monolayers of thiols.

(14) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.,* in press.

(15) Chidsey, C. E. D.; Loiacono, D. N.; Sleater, T.; Nakahara, S. *Surf. Sci.* **1988,** *200,* 45–66.

(16) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946,** *1,* 513–538.

(17) Riddes, P. W.; Blakeley, R. L.; Zerner, B. *Methods Enzymol.* **1983,** *91,* 49–60.

Preparation of Monolayers.[18] The gold-coated wafers were cut into slides (ca. 1 cm × 3 cm), rinsed with ethanol, and blown dry with a stream of argon before being immersed in the solutions of thiols and/or disulfides overnight at room temperature. These solutions were freshly prepared in deoxygenated, absolute ethanol. The mole fractions of the two adsorbates were varied while the total concentration of sulfur-terminated chains in the solution was kept constant at 1 mM. The disulfide was counted at twice its actual concentration since each molecule contributes two chains to the monolayer. The upper limit of $[R_2S_2]/[RSH]$ is limited by the solubility of the disulfide and by the concentration of thiol needed to form a high-quality monolayer. The contact angles on monolayers adsorbed from mixtures of thiols or mixtures of disulfides were unchanged after immersion in the solutions of the adsorbates for an additional month. Upon prolonged immersion in solutions containing mixtures of a thiol and a disulfide, the mole fraction of the component in the monolayer derived from the thiol, as indicated by the contact angles, gradually increased.[19]

Thiol–disulfide interchange[20] might, in principle, scramble the oxidation states of the organosulfur moieties in mixtures of thiols and disulfides. These reactions are particularly rapid in the presence of base. A 100:1 solution of $[S(CH_2)_{10}CH_3]_2$ and HS-$(CH_2)_{10}CH_2OH$ in ethanol was prepared, and two gold slides were immersed in the solution, one immediately after preparation and one 10 h later. The observation that the contact angle of water was the same on both slides indicated that thiol–disulfide interchange had not occurred to any significant extent. Similarly, we saw no evidence of disproportionation of the mixed disulfide.[21]

Contact Angles. Advancing contact angles of hexadecane and water were measured by the sessile drop technique, described in detail previously,[6] in which a drop was formed on the end of a hydrophobic, blunt-ended needle. The needle was lowered until the drop touched the surface, and the needle was then removed. A Rame-Hart Model 100 goniometer was employed to measure the contact angles.

X-ray Photoelectron Spectroscopy. XPS spectra were obtained on a Surface Science Instruments Model SSX-100 spectrometer using monochromatized Al Kα radiation. O(1s) photoelectrons were collected from each sample with an X-ray spot size of 1 mm, a pass energy of 100 eV, and an acquisition time of approximately 40 min. Within each set of experiments all the samples were examined sequentially. No change in spectrometer performance was observed during the series of analyses. The spectrum for the monolayer composed of the pure methyl-terminated species was subtracted from the other spectra, and the oxygen peak was then fit with a symmetrical 90% Gaussian/10% Lorentzian curve. The mole fraction of the hydroxyl-terminated species was calculated by normalizing the intensity of the O(1s) peak to the peak obtained from the monolayer of the pure alcohol-terminated species. When the samples in a given experiment are run automatically, the greatest error in the determination of the surface composition arises from small variations in the vertical position of the samples with respect to the focal plane of the spectrometer. If the samples are focused individually, the error in the peak area is reduced. A typical relative error in the O(1s) peak area was $\sigma = 3\%$ (for eight samples adsorbed from a 60% $HS(CH_2)_{10}CH_2OH/40\%$ $HS(CH_2)_{10}CH_3$ solution and run automatically).

S(2p) spectra of the monolayers were acquired with 50-eV pass energy, 300-μm spot, anode power of 200 W, and 115 scans (approximately 3-h acquisition time). The X-ray spot was moved
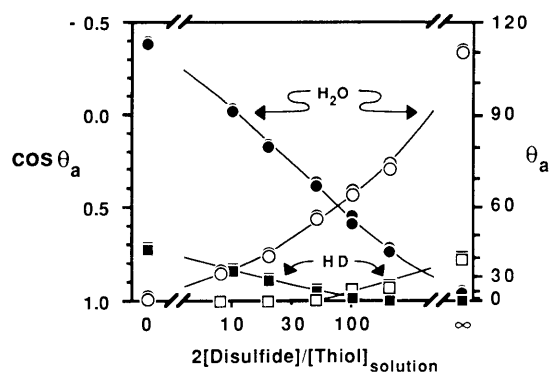

Figure 1. Advancing contact angles of water (circles) and hexadecane (squares) on monolayers formed on gold from mixtures of thiols and disulfides in ethanol: $HS(CH_2)_{10}CH_2OH + [S(C$-$H_2)_{10}CH_3]_2$ (open symbols); $HS(CH_2)_{10}CH_3 + [S(CH_2)_{10}CH_2OH]_2$ (solid symbols).
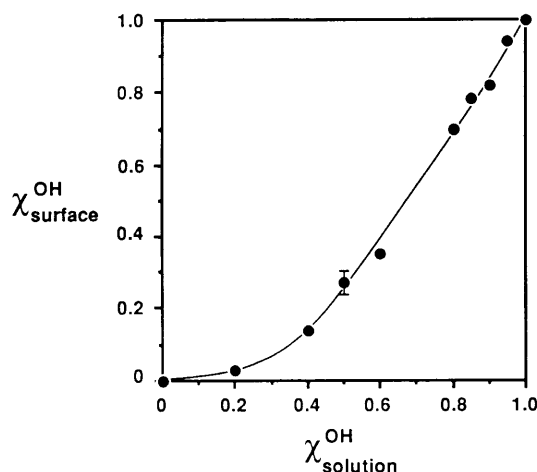

Figure 2. Mole fraction of alcohol-terminated chains in the monolayer as a function of the composition of the solution, for the coadsorption of $[S(CH_2)_{10}CH_3]_2$ and $[S(CH_2)_{10}CH_2OH]_2$ from ethanol. The compositions of the monolayers were determined by XPS. A typical error bar is shown.

to a new position on the sample after every 30 scans to minimize the effects of beam-induced damage. The spectra of the monolayers were referenced to $Au(4f_{7/2})$ at 84.0 eV. The spectra of the crystalline samples of docosanethiol, diundecyl disulfide, and the polymeric gold hexadecyl thiolate were acquired for 25 scans with a 50-eV pass energy, 300-μm spot, 50-W anode power, and 2-eV flood gun to counteract charging of the samples. They were referenced to C(1s) at 284.7 eV. Reduction of gold thiolates is very facile, and the spectra of gold hexadecyl thiolate may be influenced by electron beam induced reduction.[22] The XPS spectra are displayed unsmoothed.

Results

Figure 1 plots the advancing contact angles of water and hexadecane against the composition of the solution for monolayers assembled from mixtures of $HS(CH_2)_{10}CH_2OH + [S(CH_2)_{10}CH_3]_2$ and from $HS(CH_2)_{10}CH_3 + [S(CH_2)_{10}$-$CH_2OH]_2$. The cosine scale emphasizes the changes in interfacial energy with composition.[23] The disulfide was counted at twice its actual concentration because each molecule contributes two chains to the monolayer. The contact angles indicate a strong preference for adsorption of the thiol relative to the disulfide. If, to a first ap-

(18) Full experimental details may be found in: Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365–385. Reference 6 also.

(19) Between a 1-day and 1-month immersion, the contact angle of water on the monolayers adsorbed from mixtures of $HS(CH_2)_{10}CH_3$ and $[S(CH_2)_{10}CH_2OH]_2$ increased by 5–16°, and from $HS(CH_2)_{10}CH_2OH$ and $[S(CH_2)_{10}CH_3]_2$ decreased by 3–17°, with the greatest change occurring in solutions containing very small amounts of thiol. After 1 month the apparent preference for adsorption of a thiol was close to 200:1, although this number may be influenced by displacement of molecules in the fully formed monolayer by thiols and disulfides in solution.

(20) Szajewski, R. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 2011–2026. Whitesides, G. M.; Lilburn, J. E.; Szajewski, R. P. *J. Org. Chem.* **1977**, *42*, 332–338.

(21) No symmetrical disulfides were detectable by TLC in a concentrated solution of the mixed disulfide in ethanol 3 h after preparation.

(22) The $Au(4f_{7/2})$ peak was observed at 84.2 eV, an energy that is very close to the bulk gold peak at 84.0 eV.

(23) Young's equation relates the liquid–vapor, solid–vapor, and solid–liquid interfacial free energies to the contact angle: $\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$.
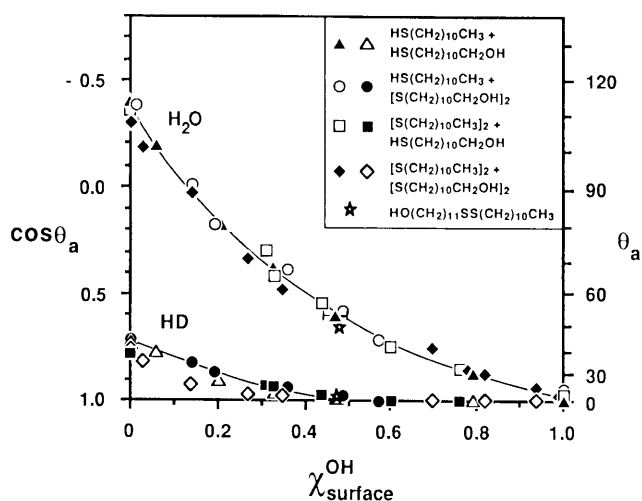
Figure 3. Contact angles of water and hexadecane on monolayers comprising mixtures of methyl- and alcohol-terminated chains. The monolayers were adsorbed onto gold from solutions containing mixtures of $HS(CH_2)_{10}CH_2OH$ and $HS(CH_2)_{10}CH_3$ (triangles), $HS(CH_2)_{10}CH_2OH$ and $[S(CH_2)_{10}CH_3]_2$ (squares), $HS(CH_2)_{10}CH_3$ and $[S(CH_2)_{10}CH_2OH]_2$ (circles), $[S(CH_2)_{10}CH_3]_2$ and $[S(C-H_2)_{10}CH_2OH]_2$ (diamonds), and a pure solution of $HOCH_2(C-H_2)_{10}SS(CH_2)_{10}CH_3$ (star). The errors in contact angle are within the symbols; a typical error in composition is shown.
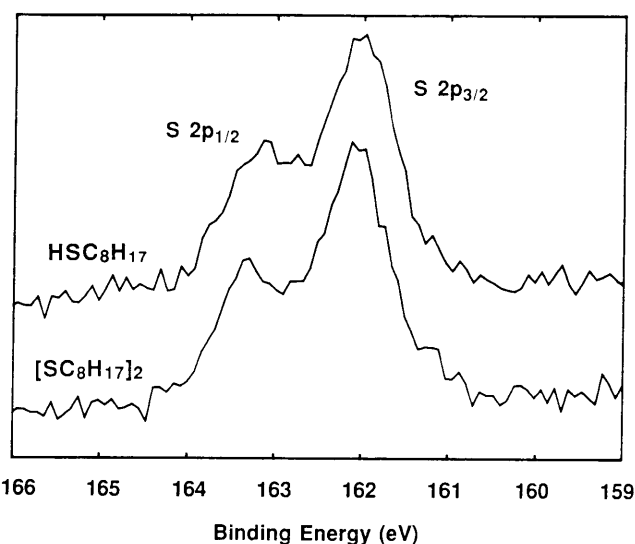

Binding Energy (eV)

Figure 4. High-resolution XPS spectra of the S(2p) photoelectrons from monolayers of octanethiol (upper spectrum) and dioctyl disulfide (lower spectrum) on gold. The spectra were acquired with a pass energy of 50 eV and a spot size of 300 μm.

proximation, we assume constant preferences, independent of the composition of the solution, for the adsorption of a thiol over its disulfide, and for one tail group over the other, then the contact angle curves for the two systems intersect at a composition representing the degree to which adsorption of the thiol was preferred: in this case 75:1 over the disulfide (see Appendix). The composition of the surface at this point was 60% methyl and 40% alcohol, indicating preferential adsorption of the methyl-terminated over the hydroxyl-terminated species.

Figure 2 plots the mole fraction of the hydroxyl-terminated species in the monolayer, determined by XPS, against the mole fraction in solution[24] for the competitive adsorption of the two disulfides, $[S(CH_2)_{10}CH_3]_2$ and $[S-(CH_2)_{10}CH_2OH]_2$, from ethanol. As with the thiol–thiol[13] and thiol–disulfide systems, adsorption of the methyl-terminated species was favored.[25] The hydroxy-terminated disulfide was particularly disfavored at low mole fractions. We have previously postulated that this behavior may arise from poor hydrogen-bonding of the OH groups in a methyl-rich surface.[14]

Clearly there is a strong preference for adsorption of an alkanethiol over the corresponding disulfide. The central question is whether this preference for thiols is kinetic or whether it arises from differences between the energies of the surface species produced by adsorption of thiols and disulfides. One way to approach this question is to look for differences in the monolayers formed from thiols and disulfides. Figure 3 is a plot of the advancing contact angles of water and hexadecane against the mole fraction of the hydroxyl-terminated chain in the monolayer. Data are shown for the three systems presented in Figures 1 and 2, for the competitive adsorption of $HS(CH_2)_{10}CH_2OH$ and $HS(CH_2)_{10}CH_3$ published previously,[14] and for the unsymmetrical disulfide $HO(CH_2)_{11}SS(CH_2)_{10}CH_3$. The contact angles for each of the two liquids fall on the same

curve to within the experimental error in the determination of the composition of the monolayer. Thus, the wettability of a monolayer comprising a particular mixture of methyl- and hydroxyl-terminated chains is independent of the species used in its formation, to within experimental error.

The nature of the species on the surface was also probed by XPS. Figure 4 shows high-resolution spectra of the S(2p) photoelectrons from monolayers of octanethiol and dioctyl disulfide.[26] The monolayers yield indistinguishable spectra, with the $S(2p_{3/2})$ peak at 162.0 eV. This peak has previously been assigned to a thiolate moiety.[11] For comparison, the $S(2p_{3/2})$ peak in the XPS spectrum of docosanethiol (freshly recrystallized from ethanol) appeared at 163.3 eV and of didocosyl disulfide at 163.0 eV. The $S(2p_{3/2})$ in polymeric gold(I) hexadecyl thiolate appeared at 162.5 eV.
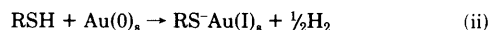
Discussion

The competitive adsorption of thiols and disulfides on gold from solution in ethanol shows a strong preference (ca. 75:1) for adsorption of thiols over disulfides. XPS spectra of the sulfur bound to the gold suggest that both adsorbates yield the same species on the surface, probably a gold thiolate ($RS^-Au(I)$), though the mechanism by which a thiol is converted to a thiolate and loses the S–H proton on adsorption is not clear.[27] Similarly, the advancing contact angles on the mixed monolayers are not sensitive to the origin of their constituent components, suggesting that monolayers formed from thiols and disulfides are structurally similar and hence that thermodynamic differences between the adsorbed species are small. If the thiols and disulfides give rise to the same species on the gold surface, then the preferential adsorption of thiols must

---

(24) For clarity we have omitted the solvent in the calculation of the mole fraction in solution.

(25) We note, however, that the composition of the monolayer is strongly dependent on the nature of the solvent. For example, in iso-octane, adsorption of the hydroxyl-terminated thiol was strongly preferred from a mixture of the two thiols.

(26) An 8-carbon chain gave a stronger sulfur signal than the 11-carbon chains used in the other experiments and hence reduced the acquisition times required.

(27) The conversion of an alkanethiol, RSH, to an alkyl thiolate, RS⁻, might plausibly involve oxidation by O_2 (eq i) or loss of H_2 (eq ii)

$$RSH + Au(0)_s + \tfrac{1}{2}O_2 \rightarrow RS^-Au(I)_s = \tfrac{1}{2}H_2O \qquad (i)$$

$$RSH + Au(0)_s \rightarrow RS^-Au(I)_s + \tfrac{1}{2}H_2 \qquad (ii)$$

In these equations, $Au(0)_s$ and $Au(I)_s$ represent surface gold atoms in formal 0 and +1 oxidation states.

be a kinetic phenomenon.[28] If adsorption of the thiol were preferred thermodynamically but adsorption of disulfides and displacement of surface thiolates by disulfides were faster, the resulting monolayer would be derived largely from the disulfide. The preference for adsorption of the thiol is much too great to arise simply from differing diffusion rates. Either the enthalpy of activation for chemisorption of the thiol is significantly lower than for the disulfide or adsorption of the disulfide is stericaly disfavored. The results obtained by Dubois et al.[11] for adsorption in UHV suggest that the latter explanation is more probable. Chemisorption of the disulfide presumably proceeds with scission of the S–S bond since a second peak arising from the intact disulfide was not observed by XPS. In solution, disulfides have a preferred conformation with a 90° CSSC dihedral angle; the conformation with a 0° CSSC dihedral angle is less favorable by at least 7 kcal/mol.[29] Sterically, approach of the S_2 moiety of the disulfide must be difficult, especially when the alkyl groups are large and the formation of the monolayer is significantly advanced. In partial monolayers, the presence of two chains and the need for adjacent unoccupied coordination sites on the gold surface might further disfavor adsorption of disulfides compared to thiols.

Although the advancing contact angles of water and hexadecane on the two-component surfaces were, to within experimental error, independent of the source of the adsorbed species, there are still subtle differences between monolayers of thiols and disulfides. For the pure methyl-terminated monolayers, in which there is no error associated with the composition of the monolayer, the contact angles were slightly lower on monolayers of disulfides than thiols. This difference was particularly marked $(\Delta\theta_a(HD) = 4°$ for diundecyl disulfide) in the contact angles of hexadecane, which are more sensitive than the contact angles of water to structural order in hydrophobic surfaces. Lower contact angles of hexadecane can result from disorder in hydrocarbon surfaces.[30] Disorder in monolayers of disulfides could plausibly reflect the difficulty of inserting the last few percent of the molecules into the monolayer. Adsorption of disulfides under different conditions and from other solvents will be discussed in a subsequent paper.

The monolayer formed by the mixed disulfide $HOCH_2(CH_2)_{10}SS(CH_2)_{10}CH_3$ provides a useful reference. The composition of the monolayer determined by XPS (48 ± 2% alcohol-terminated chains) was close to the expected value of 50% and gives us confidence in the applicability of XPS as an analytical technique for determining the composition of the surface. The contact angle of water on the mixed disulfide was slightly lower ($\sim5°$) than on the corresponding monolayers adsorbed from two-component solutions, possibly reflecting better dispersion of the two components in the monolayer formed from the mixed disulfide. Previous studies on mixed monolayers of thiols on gold have not been consistent with the segregation of the components of the monolayer into discrete domains.[9,14] We infer that none of these two-component monolayers formed islands.[31]

Conclusion

Our observations of monolayers on gold formed by adsorption from solution of thiols, disulfides, and mixtures of the two components are consistent with a model in which both precursors give rise to the same chemical species on the surface but in which the degree of perfection of the monolayers may differ. In the competitive adsorption of thiols and disulfides, the thiol was preferred by a factor of $\sim75:1$ over the disulfide. This preference for the thiol could arise from smaller steric hindrance to the approach of the molecules to the surface, from a lower activation entropy of adsorption, or possibly from differences in the rates of conversion of the initially physisorbed species to the chemisorbed thiolate.

Thiols and disulfides are both species that offer convenient control over the wettability of surfaces. It is clear, however, that disulfides must be rigorously purified to exclude contaminating thiols in order to obtain reliable results. Even at levels of contamination of less than 1%, a considerable fraction of the adsorbed monolayer on gold may be derived from the thiol.

Appendix

Let $R' = CH_3(CH_2)_{10}$ and $R'' = HO(CH_2)_{11}$. Assume that a thiol is adsorbed K_1 times faster than its disulfide, independent of the concentrations in solution or the coverage of the surface, and that a methyl-terminated species in adsorbed K_2 times faster than the hydroxyl-terminated species with the same head group. Then, for mixtures of $R'SH$ and R''_2S_2

$$\frac{[R'S]_{surf}}{[R''S]_{surf}} = K_1 K_2 \frac{[R'SH]_{sol}}{2[R''_2S_2]_{sol}} \tag{1}$$

and for mixtures of $R''SH$ and R'_2S_2

$$\frac{[R'S]_{surf}}{[R''S]_{surf}} = \frac{K_2}{K_1} \frac{2[R'_2S_2]_{sol}}{[R''SH]_{sol}} \tag{2}$$

Now assume, as we show in this paper, that the curves of the contact angles for the two systems intersect when the compositions of the monolayers are the same. Then, equating (1) and (2) and dropping the distinction between R' and R''

$$2\frac{[R_2S_2]_{sol}}{[RSH]_{sol}} = K_1 \tag{3}$$

At these concentrations in solution, the composition of the monolayer yields K_2.

$$\frac{[R'S]_{surf}}{[R''S]_{surf}} = K_2 \tag{4}$$

(28) Whether the step whose rate differentiates the thiol from the disulfide is an initial physisorption or the subsequent chemisorption/redox process that generates the surface thiolate is not established by these experiments.

(29) Dixon, D. A.; Zeroka, D.; Wendoloski, J. J.; Wasserman, Z. R. *J. Phys. Chem.* **1985**, *89*, 5334–5336.

(30) Bain, C. D.; Whitesides, G. M., unpublished results.

(31) By islands we mean single-component domains that are sufficiently large that the properties of the molecules in those islands are indistinguishable from those in a pure monolayer of the same component. We do not exclude small clusters of molecules of one type.