

Comparisons of Self-Assembled Monolayers on Silver and Gold: Mixed Monolayers Derived from HS(CH₂)₂₁X and HS(CH₂)₁₀Y (X, Y = CH₃, CH₂OH) Have Similar Properties¹

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This paper describes the preparation of self-assembled monolayers (SAMs) by adsorption of alkanethiols on evaporated silver, and compares these SAMs with analogous SAMs prepared on gold. The work concentrated on SAMs derived from mixtures of alkanethiols having long and short chains and terminating in hydrophobic and hydrophilic tails: HS(CH₂)₁₀CH₃, HS(CH₂)₂₁CH₃, HS(CH₂)₁₀CH₂OH, and HS(CH₂)₂₁CH₂OH. The thickness and the compositions of these SAMs were established by X-ray photoelectron spectroscopy (XPS). As is observed with self-assembled alkanethiolate monolayers on gold, the composition of the monolayers parallels but does not equal the solution composition. Less pronounced differences are observed between compositions in solution and on the surface on silver than have previously been reported on gold. Rates of exchange of surface thiolates with thiols in solution are similar on silver and gold. This similarity suggests that the differences between the compositions of the mixed SAMs formed from solutions having the same composition by adsorption on silver and gold are due to factors important during the initial formation of these monolayers, rather than during their subsequent equilibration. Although mixtures of thiols are probably not adsorbed in a completely random fashion on silver, no evidence could be found for the formation of discrete, separate phases on the surface (i.e., islands). Measurements of surface wettability (via contact angle measurement with water and hexadecane) exhibit departures from Cassie's expression, indicating appreciable disorder in the hydrocarbon chains at the monolayer/liquid interface. The wettability of SAMs on silver by water and hexadecane were similar to those formed on gold having the same composition.

Introduction

This paper describes methods of controlling the wettability and thickness of thin organic films (self-assembled monolayers, SAMs²) adsorbed on silver. These SAMs were derived from solutions containing mixtures of two alkanethiols, one having a chain length longer than the other. We have previously described our studies of these systems adsorbed on gold.³⁻⁵ Here we extend these studies to SAMs on silver and contrast the properties of these films with those formed on gold. Alkanethiolate monolayers formed on gold and silver have related but different structures;⁶⁻⁹ they may exhibit different macroscopic properties. Wetting is a property that is sensitive to microscopic changes

in composition,¹⁰⁻¹² morphology,¹³ and functionality.^{2,14-17} In this paper, we examine the response of wetting to the structural differences present in mixed SAMs on silver and gold.

Long-chain alkanethiols (HS(CH₂)_nX) adsorb from solution onto silver^{6-9,14} and gold¹⁴⁻²⁴ surfaces and form oriented, densely packed monolayers. On both gold and silver, the hydrocarbon chains have been shown by

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polarized infrared external reflectance spectroscopy (PIERS) to be largely trans-extended and highly crystalline^{6-8,18,20} although both theory^{25,26} and experiment^{6,20-22} indicate that gauche conformers exist and are concentrated at the terminal C-C bonds. The monolayers are, however, structurally slightly different: on gold,^{6,18,20} the axis of the hydrocarbon chain is canted at an angle of $\sim 27^\circ$ relative to the surface normal;²⁷ on silver,⁶⁻⁹ the alkanethiolate chain is canted $\sim 12^\circ$ relative to the surface normal. The cant angles are believed to result from interchain spacings that are imposed on the monolayer by the metal/sulfur lattice.^{6,28} The packing density of alkyl thiolates is greater on silver than on gold, and a much lower population of gauche conformers is present on silver at room temperature than on gold.⁶

On both silver and gold, a variety of tail groups can be accommodated in the SAMs.^{2,14-16,20} These surfaces can be hydrophobic ($\theta_a^{\text{H}_2\text{O}} \approx 115^\circ$ for X = CH₃ and CF₃) or hydrophilic ($\theta_a^{\text{H}_2\text{O}} < 15^\circ$ for X = OH, CO₂H, and CONH₂); intermediate values of wettability can be obtained by employing tail groups of intermediate polarity (for example, X = CO₂CH₃, Cl, and CN) or by generating surfaces composed of a mixture of hydrophobic and hydrophilic tail groups.^{12,14} We have recently compared the wetting properties of SAMs on silver and gold derived from HS-(CH₂)_nX, and from mixtures of HS(CH₂)₁₁CH₃ and HS(CH₂)₁₁OH; we found no differences in wetting that could be attributed to differences in the structure of the SAMs.¹⁴ The difference in the structure of SAMs of alkyl thiolates on gold and silver has not yet been shown to cause a difference in their properties.²⁹

The objective of this work was to search for such a difference using a property—wettability—in a system in which wetting has been demonstrated repeatedly to be sensitive to small variations in the structure of the SAM at its interface with liquid.^{3-5,30} The most sensitive system presently available—SAMs derived from mixtures of two *n*-alkanethiols having different chain lengths—has allowed detection of changes in surface composition and order by wetting.³⁻⁵ On gold, these systems do not form macroscopic islands (although they may form small phase-separated clusters of thiolates of the same species) and appear by IR spectroscopy to present a disordered structure at the solid-vapor interface while the bulk of the underlying monolayer remains crystalline.³¹

We examined mixed monolayers on silver derived from four *n*-alkanethiols: HS(CH₂)₁₀CH₃, HS(CH₂)₁₀CH₂OH, HS(CH₂)₂₁CH₃, and HS(CH₂)₂₁CH₂OH. We refer to these compounds, when components of SAMs, by the termini of the shorter and longer thiols (for *n* = 10, Sh = short; *n* = 21, Lg = long); for example, Sh = CH₂OH/Lg = CH₃ refers to monolayers derived from mixtures containing HS(CH₂)₁₀CH₂OH and HS(CH₂)₂₁CH₃. The differences

in the chain lengths and tail groups of the adsorbates provide easily detectable differences in thickness and wettability. This paper compares the wettability of mixed SAMs derived from mixtures of these compounds on silver and gold, and uses these data to infer comparative details of their structures.

The systems formed on gold are dynamic, and the surface composition of the monolayer increases in the longer alkanethiol with continued exposure to the contacting solution.^{4,5} We standardized our adsorption times (1 day) and concentrations (1 mM as the sum of the concentrations of all thiols in solution) to allow direct comparison with results obtained on gold under these conditions. We also examined the surface compositions formed from longer adsorption times. To allow analysis of differences in the adsorption characteristics on silver and gold, we compared the rates of exchange of surface thiolates on gold and silver with thiols in solution.

For the four sets of mixed monolayers studied, we reference both the XPS and wetting data to compositions of thiols in solution, since these compositions represent the primary experimental data. We plot wetting data as $\cos \theta$ since $\cos \theta$ is linearly related to the interfacial free energy by Young's equation³² (eq 1). We also compare

$$\cos \theta = \frac{\gamma_{\text{SV}} - \gamma_{\text{SL}}}{\gamma_{\text{LV}}} \quad (1)$$

the wettability of the monolayers with their surface composition (χ_n = surface mole fraction of component *n*). Wetting, expressed as $\cos \theta$, has been related to the composition of heterogeneous surfaces by Cassie¹⁰ (eq 2) and Israelachvili and Gee¹¹ (eq 3) where f_1 and f_2 are the

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2)$$

$$(1 + \cos \theta)^2 = f_1(1 + \cos \theta_1)^2 + f_2(1 + \cos \theta_2)^2 \quad (3)$$

fractional areas occupied by components 1 and 2, and θ_1 and θ_2 are the wetting properties of pure surfaces of 1 and 2. The adsorbates we employ can occupy different relative areas of the surface, and values of f_n and χ_n may be related but different.

Methods

Determination of the Surface Composition of Two-Component SAMs. The ratio of alkyl thiolates in a mixed SAM is often different from the ratio of thiols in the solution from which it was formed.^{3-5,12,14} To determine the surface composition (χ_n), we assume that the thickness (*d*) of a monolayer composed of two alkyl thiolates is a simple weighted average of the thicknesses of SAMs derived from the individual thiols (eq 4, Sh = shorter thiolate; Lg = longer thiolate). Equation 4 assumes

$$d = \chi_{\text{Sh}} d_{\text{Sh}} + \chi_{\text{Lg}} d_{\text{Lg}} \quad (4)$$

that the packing density of alkyl thiolates does not change with surface composition; tail groups commensurate in size with the polymethylene chain (e.g., CH₃ and CH₂OH) should have no effect on the packing density of the monolayer.²⁰ We estimate the surface composition by comparing the thickness of a mixed monolayer to the thicknesses of SAMs derived from the individual components (eq 5).³³

$$\chi_{\text{Lg}} = \frac{d - d_{\text{Sh}}}{d_{\text{Lg}} - d_{\text{Sh}}} \quad (5)$$

Relationship between Thickness of Alkanethiolate Monolayers on Silver and ln(C(1s)/Ag(3d)). Thicknesses of SAMs

(25) (a) Harris, J.; Rice, S. A. *J. Chem. Phys.* **1988**, *89*, 5898-5908. (b) Hautman, J.; Klein, M. L. *J. Chem. Phys.* **1989**, *91*, 4994-5001.

(26) Hautman, J.; Klein, M. L. *J. Chem. Phys.* **1990**, *93*, 7483-7492.

(27) Samant et al.²⁴ have estimated the tilt angle of dicosyl thiolate on Au(111) by X-ray diffraction to be $12 \pm 1^\circ$. This value has been disputed by Fenter et al.⁹ who also used X-ray diffraction but obtained tilt angles close to values^{6,18,20} obtained by infrared spectroscopy ($\sim 27^\circ$).

(28) (a) Ulman, A.; Eilers, J. E.; Tillman, N. *Langmuir* **1989**, *5*, 1147-1152. (b) Bareman, J. P.; Klein, M. L. *J. Phys. Chem.* **1990**, *94*, 5202-5205.

(29) Ulman et al. (Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir* **1989**, *5*, 101-111.) have reported differences in the wettability of SAMs on silver and gold derived from HS(CH₂)₁₁OH ($\theta_a^{\text{H}_2\text{O}} \approx 20$ and $< 10^\circ$, respectively). We observed that SAMs derived from HS(CH₂)₁₁OH on gold and silver under controlled, anaerobic conditions exhibit common wetting properties ($\theta_a^{\text{H}_2\text{O}} = 10-15^\circ$).¹⁴

(30) (a) Hugh, D. B. *Adv. Colloid Interface Sci.* **1980**, *14*, 3-14. (b) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897-5898. (c) Wilson, M. D.; Ferguson, G. S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 1244-1245.

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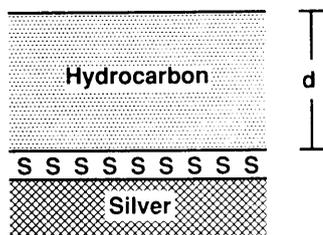


Figure 1. Schematic illustration of an *n*-alkanethiolate monolayer adsorbed on silver.

have been estimated by a variety of techniques.³⁴ For these systems on silver, we find X-ray photoelectron spectroscopy (XPS) to be a convenient and highly reproducible method of estimating the thicknesses of the SAMs. We estimate thicknesses by comparing the intensity of peaks due to C(1s) and Ag(3d) and relate these thicknesses to surface compositions using eq 5. Figure 1 is a schematic illustration of an alkanethiolate monolayer on silver. The XPS intensities of the C(1s) and Ag(3d) peaks can be described by eqs 6 and 7, where C_d is the intensity of the C(1s)

$$C_d = C_\infty - e^{-d/\lambda_1 \sin \phi} \quad (6)$$

$$Ag_d = Ag_\infty S(e^{-d/\lambda_2 \sin \phi}) \quad (7)$$

photoelectrons due to the monolayer of thickness d ; Ag_d is the intensity of the Ag(3d) photoelectrons attenuated by the alkanethiolate monolayer of thickness d ; C_∞ and Ag_∞ are the intensities of photoelectrons (C(1s) and Ag(3d), respectively) expected for infinitely thick layers of hydrocarbon and silver, respectively; d is the thickness of the hydrocarbon portion of the monolayer; λ_1 and λ_2 are the attenuation lengths of photoelectrons due to C(1s) and Ag(3d) through a hydrocarbon film, respectively—we estimate these parameters to equal 35 and 34 Å, respectively;³⁵ ϕ is the angle between the analyzer and the surface (the take-off angle here is 35°); S is a term that corrects the silver signal for attenuation by the adsorbed sulfur.

Taking the logarithm of the ratio of eqs 6 and 7 yields eq 8 where the constant $K = \ln(C_\infty/Ag_\infty S)$. The constant contains terms that are dependent on instrumental parameters, and its value is not important for our analysis. Equation 8 is composed

$$\ln(C_d/Ag_d) = d/(\lambda_2 \sin \phi) + \ln(1 - e^{-d/\lambda_1 \sin \phi}) + K \quad (8)$$

of a term linear in thickness and a term that remains approximately constant at sufficiently high values of d to have a negligible effect on the "slope" of the function. Figure 2 contains a plot of the function given in eq 8 ($K = 1.75$) over the range of thicknesses 0–40 Å; experimental data are provided for comparison. The thicknesses of the hydrocarbon portion of the *n*-alkanethiolate monolayers were estimated by eq 9 where 1.27 Å is the incremental

$$d = 1.27n \cos \alpha \quad (9)$$

(32) Young, T. *Philos. Trans. R. Soc. London* 1805, 95, 65–87.

(33) For SAMs derived from two components, $\chi_{Sh} + \chi_{Lg} = 1$.

(34) Thicknesses of SAMs on gold have been determined by ellipsometry^{3-5,7,18} and XPS attenuation.^{6,14} Ellipsometry requires analysis of the substrate before and after exposure to the adsorbate. This analysis with gold is relatively straightforward technically, since gold does not oxidize. Silver, unlike gold, oxidizes readily and adsorbs contaminants upon exposure to air. This reactivity makes analysis difficult. We^{6,14} have also routinely estimated the relative thicknesses of the SAMs by measuring the attenuation of the XPS signal due to the underlying metal by the SAM. This method has proven successful on gold but has the disadvantage of being heavily dependent on spectrometer focus and on a stable X-ray source. It also requires an internal standard. The method we employ here avoids these complications, and we find it to be a sensitive probe of changes in thickness.

(35) The attenuation lengths of photoelectrons of kinetic energies 500–1500 eV in hydrocarbons can be readily estimated by eq 1

$$\lambda (\text{Å}) = 9.0 + 0.022KE (\text{eV}) \quad (i)$$

(Laibinis, P. E.; Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* 1991, 95, 7017–7021). The kinetic energies for photoelectrons for C(1s) and Ag(3d) from Al K α irradiation are 1202 and 1116 eV, respectively. Using eq 1, attenuation lengths of 35 and 34 Å are calculated for C(1s) and Ag(3d).

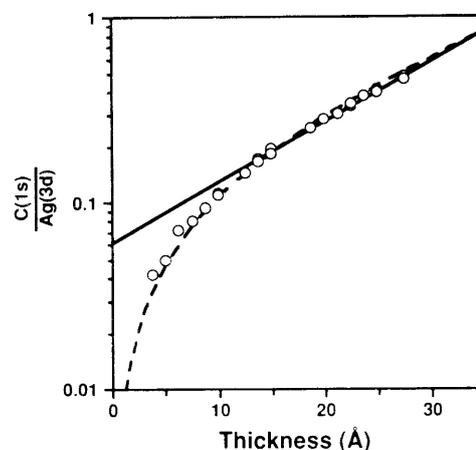


Figure 2. Relation between XPS intensities of C(1s) and Ag(3d), and thicknesses for *n*-alkanethiolate monolayers on silver. Values of C(1s)/Ag(3d) are a function of instrumental parameters; trends are important here. The dashed line displays the theoretical relation given in eq 8 using $K = 1.75$. The thicknesses of the hydrocarbon layer of the monolayers were estimated using eq 9. The solid line represents a linear least-squares fit to the data presented in the figure ($R^2 = 0.994$) for monolayers prepared from $C_nH_{2n+1}SH$ ($n = 11-22$).

length per methylene in a trans-extended hydrocarbon chain (a value derived from X-ray data for paraffins),³⁶ n is the number of carbons in the *n*-alkanethiolate, and α is the angle the hydrocarbon chain is canted relative to the surface normal ($\sim 12^\circ$) by IR.⁶⁻⁹

In this study we have employed materials that vary from 11 to 22 carbons in length (or from ~ 14 to 27 Å in thickness) of the hydrocarbon layer. From Figure 2, the relation (eq 8) between $\ln(C/Ag)$ and thickness for thicknesses varying between 14 and 27 Å is virtually linear in accord with experimental data. We thus assume that the midpoint in surface composition—which would presumably be midway in thickness between the two extremes—can be estimated from the midpoint of values of $\ln(C/Ag)$.

The systems that we study here, like all previously reported studies of mixed monolayers,^{4,5} are not at thermodynamic equilibrium. Where thermodynamic equilibrium lies in these systems remains an important unresolved question, and we have begun studying the factors—tail groups, chain lengths, metals, adsorption times, and solution concentrations—that may influence its value. We find that a useful metric against which to compare data from these systems is the ratio of the components in solution ($R_{\text{soln}} = [Sh]_{\text{soln}}/[Lg]_{\text{soln}}$) required to generate a SAM composed of an equimolar mixture of the two components ($R_{\text{SAM}} = [Sh]_{\text{SAM}}/[Lg]_{\text{SAM}} = 1$). We present data here in this fashion and compare them with adsorption data obtained on gold under similar conditions.

Results

SAMs on Silver Derived from Different Length Alkanethiols Terminating in Different Functional Groups: Sh = CH₃/Lg = CH₂OH and Sh = CH₂OH/Lg = CH₃ from Ethanol. The properties of SAMs derived from 1-day exposure of freshly evaporated silver to ethanolic solutions (1 mM in total thiol concentration) containing mixtures of two alkanethiols of different chain lengths terminating in different tail groups are given in Figures 3 and 4. For comparisons, data obtained for SAMs on gold prepared under similar experimental conditions are displayed as dotted lines in these figures. In both the Sh = CH₃/Lg = CH₂OH and Sh = CH₂OH/Lg = CH₃ systems, the wettability of SAMs on silver and gold derived from solutions containing the two components ranges between the values obtained on the pure monolayers.³⁷

(36) Abrahamsson, S.; Larsson, G.; von Sydow, E. *Acta Crystallogr.* 1960, 13, 770–774.

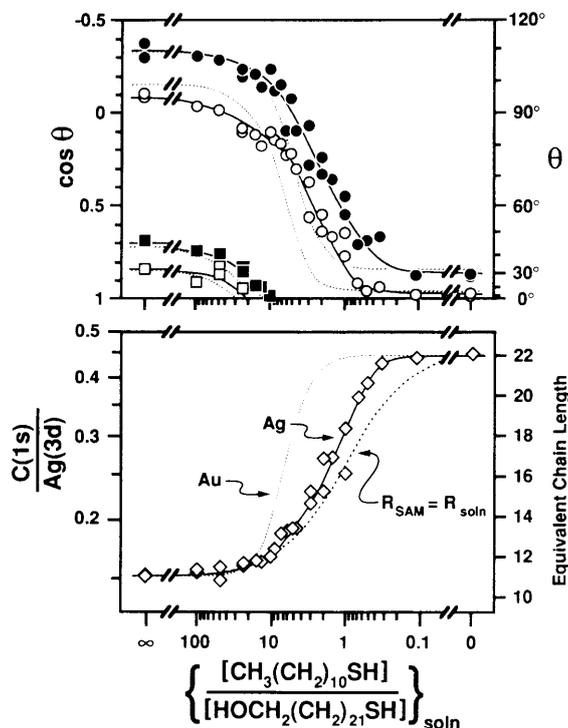


Figure 3. Monolayers on silver prepared by 1-day exposure to ethanolic solutions containing mixtures of $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ ($\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_2\text{OH}$). Solid and open symbols represent advancing and receding contact angles (θ_a and θ_r), respectively; circles and squares represent water and hexadecane, respectively. The solid lines are provided as guides to the eye. The dotted lines represent data obtained under similar conditions with SAMs on gold⁵ and are provided for comparison. The right-hand axis in the lower panel shows the equivalent chain length, n , of a pure monolayer derived from adsorption of $\text{C}_n\text{H}_{2n+1}\text{SH}$ on silver that would yield the same ratio of $\text{C}(1s)/\text{Ag}(3d)$; data on gold are scaled to the right-hand axis in a manner similar to thicknesses determined by XPS attenuation and ellipsometry data on mixed SAMs. The dashed line in the lower panel represents the adsorption profile expected if the surface composition equalled the solution composition ($R_{\text{SAM}} = R_{\text{soln}}$).

The SAMs on the two metals formed under similar conditions exhibit differences in wettability and surface composition. The surface compositions of the SAMs formed on silver are closer to the composition of the solution than are the SAMs formed on gold.

In Figure 5, we compare the wetting properties of mixed SAMs on silver and gold. The differences in the wettabilities of SAMs formed on gold and silver from common solutions (Figures 3 and 4) appear to reflect directly the differences in their surface compositions. The data from SAMs on silver and gold are remarkably similar for corresponding values of surface composition (Figure 5).

With continued exposure to a solution containing a mixture of the two thiols, the wetting properties and the compositions of the resulting SAMs change. In the $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_2\text{OH}$ system, the monolayers become more hydrophilic; in the $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_3$ system, they become more hydrophobic. XPS data confirm that the compositions of the monolayers have changed; the surface compositions increase in the longer component (see Figure 6). Similar effects have been observed on gold.^{4,5} As with

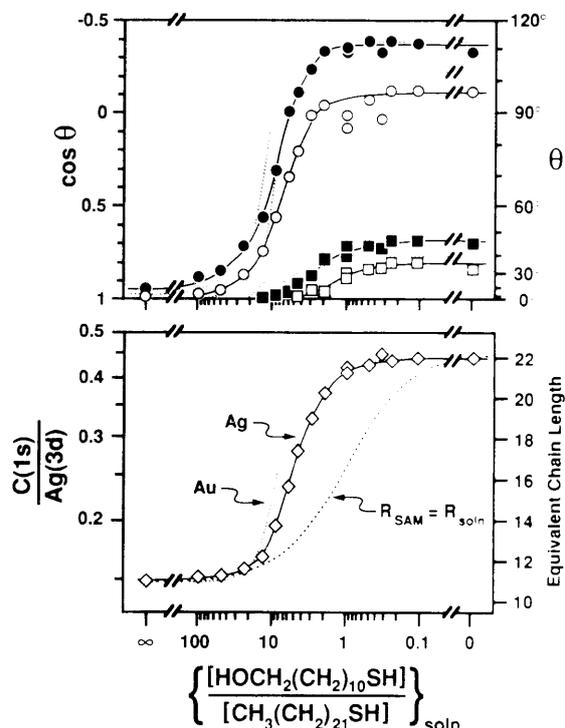


Figure 4. Monolayers on silver prepared by 1-day exposure to ethanolic solutions containing mixtures of $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ ($\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_3$). Data are presented as in Figure 3.

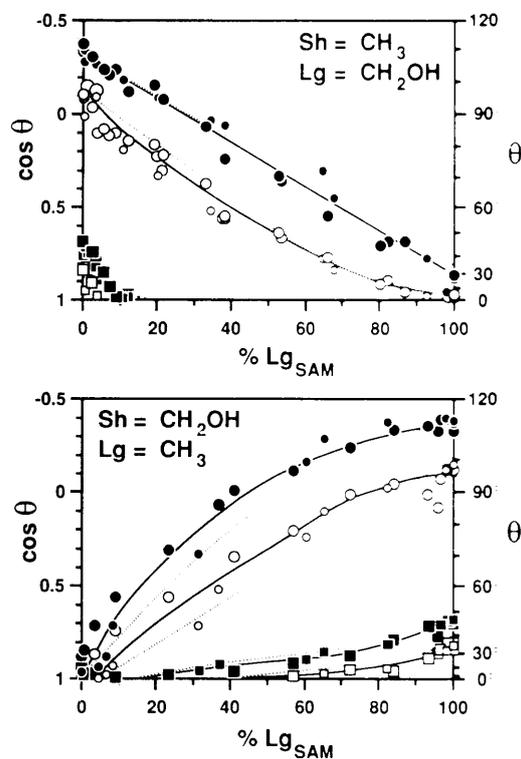


Figure 5. Wetting properties of monolayers on silver derived from mixtures of $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ ($\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_2\text{OH}$) and of $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ ($\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_3$). The surface compositions of the monolayers were estimated by XPS (see text). Larger and smaller points represent data obtained after exposure to solution for 1 day and 1 week, respectively. Solid and open symbols represent advancing and receding contact angles (θ_a and θ_r), respectively; circles and squares represent water and hexadecane, respectively. The solid lines are provided as guides to the eye; dotted lines represent data obtained on SAMs on gold⁵ and are provided for comparison.

SAMs on gold, the relation between wettability and surface composition is essentially independent of the length of

(37) The SAMs derived from pure $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ on silver and gold are not wet by water ($\theta_{\text{H}_2\text{O}} \approx 25^\circ$). SAMs derived from $\text{HS}(\text{CH}_2)_n\text{OH}$ ($n = 11, 16, 19$) have been reported^{3,14,16,17} to generate monolayers on gold and silver that are wet by water ($\theta_{\text{H}_2\text{O}} \leq 15^\circ$) while SAMs on gold derived from $\text{HS}(\text{CH}_2)_{21}\text{OH}$ are less hydrophilic ($\theta_{\text{H}_2\text{O}} \approx 20^\circ$) (Evans, S. D.; Sharma, R.; Ulman, A. *Langmuir* 1991, 7, 156-161). Although all compounds were reported to be pure by ¹H NMR, the higher molecular weight ω-hydroxyalkanethiols are more difficult to purify, and trace impurities may be responsible for the observed differences in wettability.

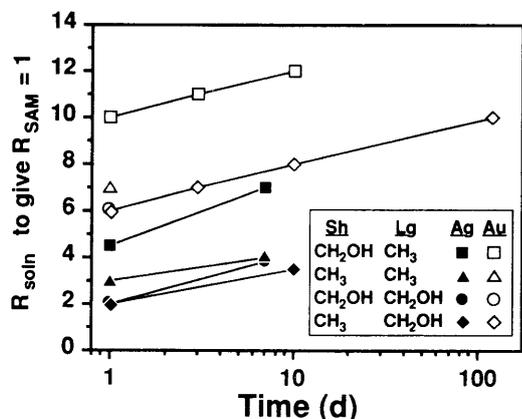


Figure 6. Ratio of two different length alkanethiols (C_{11} and C_{22}) required in ethanolic solutions to obtain SAMs of equimolar surface concentration on silver and gold as a function of length of exposure to contacting solution. The total concentration of thiols in each experiment was 1 mM. Data on gold were taken from ref 5. Lines are provided as guides to the eye. Sh and Lg refer to the tail groups of the thiols used in the adsorption: $\text{HS}(\text{CH}_2)_{10}\text{Sh}$ and $\text{HS}(\text{CH}_2)_{21}\text{Lg}$.

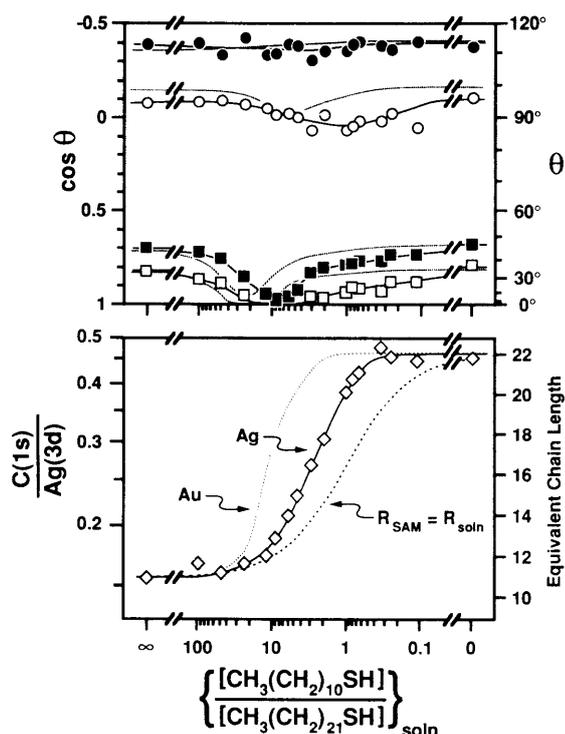


Figure 7. Monolayers on silver prepared by 1-day exposure to ethanolic solutions containing mixtures of $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ (Sh = CH_3 /Lg = CH_3). Data are presented using the conventions in Figure 3.

exposure to the contacting solution. This observation indicates that wetting is insensitive to the (we presume small) changes taking place in the structure and composition of the SAM.

SAMs on Silver Derived from Different Length Alkanethiols Terminating in Common Functional Groups: Sh = CH_3 /Lg = CH_3 and Sh = CH_2OH /Lg = CH_2OH from Ethanol. The properties of SAMs derived from exposure of silver films to ethanolic solutions containing different length alkanethiols terminating in the same tail group for 1 day (1 mM in total thiol concentration) are given in Figures 7 and 8. The data were obtained under experimental conditions similar to those reported previously on gold; the data obtained on gold are displayed as dotted lines in these figures. The wetting properties of the Sh = CH_3 /Lg = CH_3 monolayers by hexadecane, and of the Sh = CH_2OH /Lg = CH_2OH

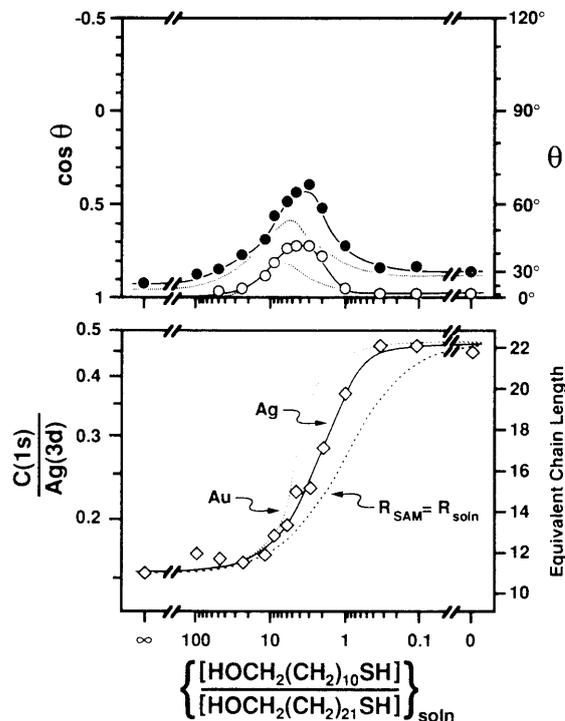


Figure 8. Monolayers on silver prepared by 1-day exposure to ethanolic solutions containing mixtures of $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ (Sh = CH_2OH /Lg = CH_2OH). Data are presented using the conventions in Figure 3.

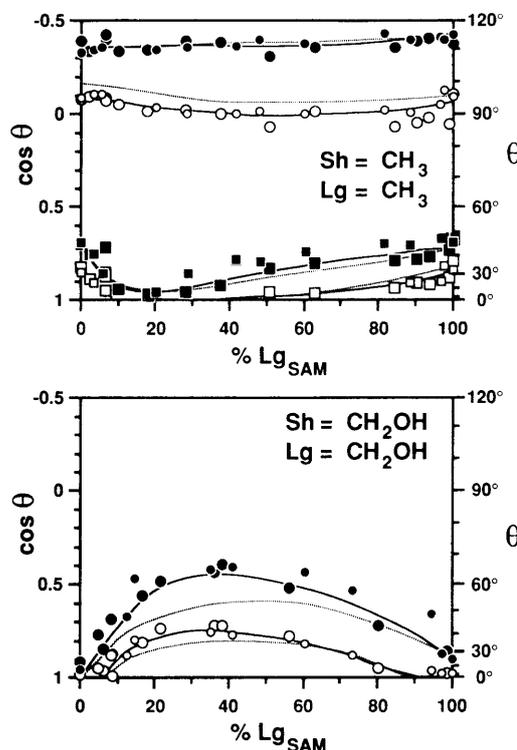


Figure 9. Wetting properties of monolayers on silver derived from mixtures of $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ (Sh = CH_3 /Lg = CH_3) and of $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ (Sh = CH_2OH /Lg = CH_2OH). Data are presented using the conventions in Figure 5.

monolayers by water, cannot be described by arithmetic sums of the interfacial energetics of the tail groups (eqs 2 and 3). These deviations require that appreciable disordering of the hydrocarbon chains occurs at the monolayer/liquid interface.

Figure 9 relates the wetting properties of the SAMs formed on silver to their surface compositions. The wetting of the mixed SAMs on silver and gold are similar, for similar

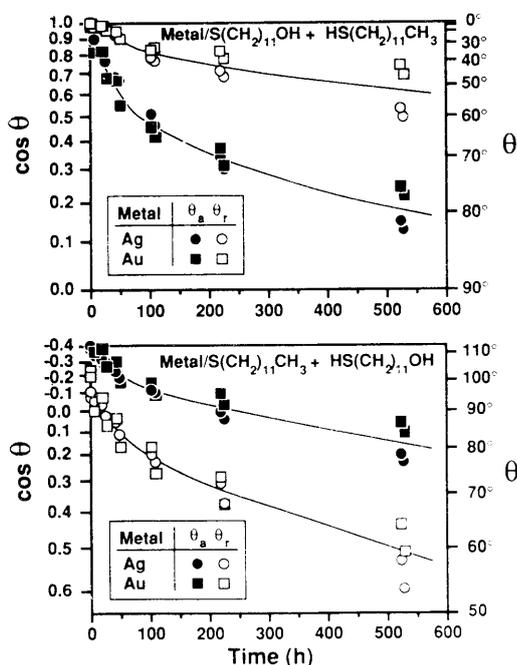


Figure 10. Exchange of metal thiolates ($M-S(CH_2)_{11}X$) with thiols ($HS(CH_2)_{11}Y$) in solution; $M = Ag, Au$; $X \neq Y = CH_3, OH$. Pure SAMs derived from $HS(CH_2)_{11}X$ were assembled on silver and gold (circles and squares, respectively) and immersed in 1 mM ethanolic solutions containing $HS(CH_2)_{11}Y$. The samples were removed from solution and the advancing and receding contact angles of water (filled and open symbols) measured. The data are plotted on a scale logarithmic in $\cos \theta$ to demonstrate that the exchange process does not follow first-order kinetics. The lines are provided as guides to the eye.

surface compositions (percent L_{GSAM}). With continued exposure to the contacting solutions, the composition of these SAMs increase in the longer component (Figure 6); the relation between wettability and surface composition, however, does not change (Figure 9).

Comparison of the Exchange of Metal Thiolates on Silver and Gold with Thiols in Solution. In the four systems of mixed SAMs studied on silver and gold, the surface compositions differed from the solution compositions and were slightly different on the two metals—SAMs on silver being closer to the composition of the solution. On both metals, the longer component is preferred in the SAMs and its surface concentration increases with continued exposure to the solution (Figure 6). We examined qualitatively the relative rates of exchange on the two metals to determine whether the differences in surface compositions on the two metals could be due to exchange processes.

We prepared pure SAMs of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$ on silver and gold. We immersed the SAMs in 1 mM ethanolic solutions of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{11}OH$, respectively, and measured their wettability by water after various intervals of exposure (Figure 10). The wetting properties of the SAMs change and can be related to the replacement of surface thiolates: the wettability of SAMs on silver and gold prepared from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$ by water is linearly related to the surface composition (eq 2).¹⁴ The rate of replacement of thiolates of one tail group with thiols of another on the two metals is approximately the same. The exchange does not follow first-order kinetics.

On both metals, the replacement of hydroxyl-terminated alkanethiolates by methyl-terminated alkanethiols is slightly faster than that of methyl-terminated alkanethiolates by hydroxyl-terminated alkanethiols (Figure 10).³⁸ Competitive adsorption experiments of these two alkanethiols for the surfaces of silver and gold from eth-

anol also show a preference on the surface for the methyl-terminated thiol.¹⁴ We do not presently have a mechanistic model that explains these preferences in detail, but we note that the methyl-terminated surfaces have lower free energies than those terminated by CH_2OH , and are more stable.

Discussion

Comparison of Properties of Mixed SAMs on Silver and Gold. The SAMs formed on silver and gold are similar but not identical in their wetting properties. Are any of the differences due to differences in the structures of the SAMs? Are the structures of the mixed SAMs—especially the in-phase distribution of components—different for the same values of R_{SAM} ?

The most pronounced difference on silver and gold is the surface composition of SAMs formed on the two metals under similar conditions (Figures 3, 4, 7, and 8). In brief, although both systems appear not to be at thermodynamic equilibrium, SAMs on silver appear to be more kinetically determined than those on gold (or, put the other way, SAMs on gold are closer to thermodynamic equilibrium than those on silver). The compositions of the SAMs on silver are closer to the composition of the solution from which they were formed than those on gold. When formed from mixtures of long and short thiols, both SAMs on gold and silver contain a higher concentration of the longer component than does the contacting solution. At equilibrium, SAMs containing the longer component would be expected to be the more stable. On both metals, the content of the longer component increases with continued exposure to solution. The SAMs on gold continue to have a higher concentration of the longer component than silver as the time for equilibration with the solution increases (Figure 6).

The differences in composition of SAMs on the two metals must reflect processes occurring during their formation.³⁹ The amount of exchange (Figure 10) that can occur during exposure to a 1 mM ethanolic solution for 1 day ($\sim 20^\circ C$) is too small to account for the observed compositions of the surface if the initially formed SAM had the composition of the solution. Essentially complete SAMs form from 1 mM solutions in seconds.¹⁶ The factors that affect the composition of the SAM are, therefore, probably important only during the assembly of the monolayer. One possibility is that the sticking coefficient of the longer alkanethiols on the metals is higher than for shorter thiols.

The chemistry of formation of alkyl thiolates on the two metal surfaces is different. Gold does not form an oxide, and its reaction with alkanethiols, though still not completely understood, probably involves oxidative addition of the thiol to gold and subsequent loss of the hydrogen as H_2 or H_2O .⁴⁰ In contrast, silver oxidizes readily. All of the silver films we have used have thin surface films of oxide before exposure to the solution of alkanethiols, and it is this oxidized surface that reacts with thiols. The resulting SAMs on silver contain no (or very little) silver oxide.⁶ The oxide must be removed during formation of the SAMs either by reduction or

(38) The change in $\cos \theta_a$, a quantity linearly related to surface composition, is greater in the upper panel of Figure 10 than the lower one.

(39) Bain et al.¹² have reported that large differences between surface and solution compositions can be produced on short time scales. Exposure of gold to a solution of $HS(CH_2)_{10}CH_3$, $HS(CH_2)_{11}OH$ (4:1; $\chi_{soln}^{OH} = 0.20$) in isoctane forms SAMs composed primarily of hydroxyl-terminated alkanethiolates ($\chi_{SAM}^{OH} > 0.95$). The composition of the SAMs derived from 1-min exposure are approximately the same as SAMs derived from 1-week exposure.

(40) For a recent mechanistic study, see: Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.*, 1991, 310, 335–359.

displacement by the thiols. The different chemistries that occur on the metal/metal oxide surfaces and not the different structures formed on the two metals are probably responsible for the different surface compositions that result on the two metal surfaces.

Relation between Wettability and the Structure and Composition of the SAM. The different tilted structures that single-component alkyl thiolate SAMs form on gold and silver are primarily a result of differences in the inter-thiolate distances that are preferred on the metal surfaces.²⁵ The cross-sectional area of a polymethylene chain is 18.4 \AA^2 .⁴¹ On Au(111) (the predominate crystallographic orientation of our polycrystalline samples), alkanethiols adsorb and form a commensurate ($\sqrt{3} \times \sqrt{3}$)- $R30^\circ$ overlayer lattice.²²⁻²⁴ The inter-thiolate distance on Au(111) (5.0 \AA) results in an area per chain (21.4 \AA^2) that is greater than the cross-sectional area of a polymethylene chain by $\sim 15\%$. As a result, the axis of the hydrocarbon chain tilts $\sim 27^\circ$ from the surface normal to maximize van der Waals contact between the chains.²⁵ The spacing of *n*-alkyl thiolate SAMs formed on Ag(111) (the predominate crystallographic orientation of our polycrystalline samples)⁶ has not yet been determined. Analogous adsorbates on Ag(111)— H_2S ⁴² and CH_3SSCH_3 ⁴³—adopt higher packing densities of thiolates than the ($\sqrt{3} \times \sqrt{3}$)- $R30^\circ$ structure formed on Au(111).^{44,45} As a result, the hydrocarbon chains should require less tilting on silver than on gold to bring the polymethylene chains into van der Waals contact. By IR and other methods, the axes of the hydrocarbon chains on silver have been found to tilt only $\sim 12^\circ$ from the surface normal.⁶⁻⁹ On both silver and gold, the structure of the metal-thiolate lattice in single-component SAMs and in the mixed SAMs studied here should be the same; the structure of the hydrocarbon region of the SAM near the metal surface should be similar to those of pure SAMs.

Figures 5 and 9 illustrate that the relation between wetting and the composition of the four sets of mixed SAMs studied on silver are extremely similar to those formed on gold ($\Delta\theta \leq 10^\circ$). In view of the differences that exist in structure between SAMs on silver and gold (and possibly also in the morphology of the supports), this similarity is remarkable. The wetting properties of the SAMs appear to be determined primarily by the *interfacial composition* of the SAMs. Differences in the details of the structure of the types provided by SAMs on silver and gold do not have a significant influence on wetting.

(41) (a) Bunn, C. W. *Trans. Faraday Soc.* **1939**, *35*, 482-491. (b) Shearer, H. M. M.; Vand, V. *Acta Crystallogr.* **1956**, *9*, 379-384. (c) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1973; Vol. 1, p 97.

(42) (a) Schwaha, K.; Spencer, N. D.; Lambert, R. M. *Surf. Sci.* **1979**, *81*, 273-284. (b) Rovida, G.; Pratesi, F. *Surf. Sci.* **1981**, *104*, 609-624.

(43) (a) Harris, A. L.; Rothberg, L.; Dubois, L. H.; Levinos, N. J.; Dhar, L. *Phys. Rev. Lett.* **1990**, *64*, 2086-2089. (b) Harris, A. L.; Rothberg, L.; Dhar, L.; Levinos, N. J.; Dubois, L. H. *J. Chem. Phys.* **1991**, *94*, 2438-2448.

(44) Methanethiolate on Ag(111), derived from adsorption of CH_3SSCH_3 , forms a ($\sqrt{7} \times \sqrt{7}$)- $R10.9^\circ$ overlayer structure.⁴³ The inter-thiolate spacing (4.42 \AA) of this structure, however, results in an area per chain ($16.9 \text{ \AA}^2/\text{RS}$) that is too small to accommodate a polymethylene chain. Two structures have been observed upon adsorption of H_2S on Ag(111): ($\sqrt{7} \times \sqrt{7}$)- $R10.9^\circ$ and ($\sqrt{39}16.1^\circ \times \sqrt{39}16.1^\circ$).⁴² This latter structure yields an area per chain of $20.3 \text{ \AA}^2/\text{RS}$, larger than the area of a polymethylene chain (18.4 \AA^2)⁴¹ and smaller than the area per chain on Au(111) ($21.4 \text{ \AA}^2/\text{RS}$).²²⁻²⁴

(45) Recent X-ray and helium diffraction studies⁹ of $\text{C}_{18}\text{H}_{37}\text{SH}$ adsorbed on Ag(111) have determined the adsorbate to be rotated 12.2° from the Ag lattice and have nearest-neighbor spacings of $\sim 4.7 \text{ \AA}$ ($\sim 19.1 \text{ \AA}^2/\text{RS}$). These parameters are inconsistent with formation of the ($\sqrt{3} \times \sqrt{3}$)- $R30^\circ$ and ($\sqrt{39}16.1^\circ \times \sqrt{39}16.1^\circ$) structures that are observed for adsorption of $\text{CH}_3(\text{CH}_2)_{21}\text{SH}$ on Au(111)²²⁻²⁴ and H_2S on Ag(111).⁴² The structures that form on Ag(111) are presumably incommensurate.⁹

Experimental Section

Materials. The alkanethiols were available from previous studies.^{4,14} Absolute EtOH (U.S. Industries), Ag wire (Aldrich; 99.99+%), W and Cr-coated W filaments (R. D. Mathis Co.), prepurified Ar (Med-tech; 99.998%, <5 ppm O_2), and dodecanethiol (Aldrich) were used as received. Si(100) wafers (100 mm, Silicon Sense) were cut into $1 \times 3 \text{ mm}$ slides, rinsed with absolute EtOH, and blown dry before use. Contacting solutions (1 mM total thiol concentration) were prepared from N_2 -purged absolute EtOH.

Preparation of Monolayers. The silver substrates were prepared in a diffusion-pumped thermal evaporator (base pressure 10^{-6} Torr). Cr (100 \AA) and Ag ($\sim 1000 \text{ \AA}$) were evaporated individually from resistively heated tungsten filaments onto pre-cut slides of Si(100). Immediately following evaporation, the chamber was backfilled with prepurified Ar. Slides were transferred to solution under a flow of Ar and were deposited into the various solutions in no set order. The backfill of the chamber and the transfer of slides to all solution (two slides per solution) in a run could be accomplished within 7 min after the conclusion of evaporation. Slides were exposed to the ethanolic solutions for 1 day or 1 week, removed from solution, washed with EtOH, and blown dry prior to analysis.

Wetting. Advancing and receding contact angles of water and hexadecane were measured on static drops that had been applied or removed at a constant flow rate ($\sim 1 \mu\text{L/s}$) using a Matrix Technologies Electro-pipette. The contact angles were measured using a Ramé-Hart goniometer; the pipet tip was not removed from the drop. Each SAM was characterized with at least three drops of liquid, and the contact angles were measured on both sides of the drop. Data presented for 1-day exposure are the average of two sets of these six measurements.

X-ray Photoelectron Spectroscopy (XPS). XPS spectra were collected on a Surface Science X-100 XPS spectrometer with a monochromatized Al $K\alpha$ source, concentric hemispherical analyzer, and multichannel detector. The spectra were accumulated at a pass energy of 100 eV and a spot size of $1000 \mu\text{m}$ and took $<10 \text{ min/slide}$. X-ray-induced damage under these conditions is negligible. The spectra were fit using 80% Gaussian/20% Lorentzian peaks.

XPS was used to measure the thickness of the mixed SAMs (eq 8). Values of $C(1s)/\text{Ag}(3d)$ were typically within $<5\%$ for SAMs derived from *n*-alkanethiols of a common chain length. SAMs exposed to an adsorbate for 1 week exhibited values of $C(1s)/\text{Ag}(3d)$ that were $\sim 10\%$ greater than those obtained after 1-day exposure.⁴⁶ In Figures 3, 4, 7, and 8, we set the values of $C(1s)/\text{Ag}(3d)$ obtained for the two pure SAMs in a particular experiment to their respective thicknesses expected from eq 9. End point values from both 1-day and 1-week exposures were within one unit of *n* of those given in Figure 2. We believe the method used here to determine thicknesses should be applicable to other systems. We recommend use of an XPS peak for the underlying substrate that has a kinetic energy similar to that of the overlayer as the relation (eq 8) between thicknesses and \ln (overlayer/underlayer) approximates linearity at lower values of thickness the closer the values of λ_1 and λ_2 are.

Exchange of Metal Thioliates with Alkanethiols in Solution. SAMs derived from $\text{HS}(\text{CH}_2)_{11}\text{X}$ ($\text{X} = \text{OH}, \text{CH}_3$) on silver and gold were prepared via 1-day exposure to 1 mM ethanolic solutions as previously described.^{6,14} The slides were removed from solution, characterized by wetting, and immersed into fresh 1 mM ethanolic solutions of $\text{HS}(\text{CH}_2)_{11}\text{Y}$ ($\text{Y} = \text{CH}_3, \text{OH}; \text{X} \neq \text{Y}$) bearing the other tail group. The slides were periodically removed from solution, characterized by wetting, and reimmersed into the solution. The data presented in Figure 10 are from two independent experiments.

Registry No. Ag, 7440-22-4; Au, 7440-57-5; $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$, 5332-52-5; $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$, 7773-83-3; $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$, 73768-94-2; $\text{HS}(\text{C}_2)_{21}\text{CH}_2\text{OH}$, 137057-24-0; hexadecane, 544-76-3.

(46) We have reported that continued exposure of alkyl thiolate SAMs on silver to thiols results in formation of a layer of Ag_2S between the SAM and Ag.⁶ We believe the increase in the value of $C(1s)/\text{Ag}(3d)$ is due to attenuation of the Ag(3d) signal by the layer of Ag_2S .