

AD-A254 901



(2)

**SELF-ASSEMBLED MONOLAYERS OF ALKANETHIOLS ON GOLD:
MONOLAYERS DERIVED FROM TWO COMPONENTS WITH ALKANE
CHAINS OF DIFFERENT LENGTHS**

John P. Folkers, Paul E. Laibinis, and George M. Whitesides
Department of Chemistry
Harvard University
Cambridge, MA 02138

Technical Report No. 50 (July 1992)

DTIC
S ELECTE D
A
SEP 03 1992

Interim Technical Report
(Accepted for publication in J. Adhes. Sci. Tech.)

PREPARED FOR DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
3701 N. Fairfax Drive
Arlington VA 22203-1714

DEPARTMENT OF THE NAVY
Office of Naval Research, Code 1130P
800 North Quincy Street
Arlington VA 22217-5000

Project No.: a400011dd205
Contract No.: N00014-86-K-0756
Effective Date: 86 September 15
Expiration Date: 92 September 30

Principal Investigator: George M. Whitesides (617-495-9430)

The views and conclusions in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U.S. Government.

This document has been approved
for public release and sale; its
distribution is unlimited.

92 9 02 274

163730

92-24566



25 PC

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 50			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Harvard University		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION DARPA	
6c. ADDRESS (City, State, and ZIP Code) Office for Sponsored Research Holyoke Center, Fourth Floor Cambridge MA 02138-4993			7b. ADDRESS (City, State, and ZIP Code) 1400 Wilson Boulevard Arlington VA 22209-2308		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) Chemistry Division, Code 1113 Office of Naval Research Arlington VA 22217-5000			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 86-K-0756	PROJECT NO.	TASK NO. a400011dd2
			WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) "Self-Assembled Monolayers of Alkanethiols on Gold: Monolayers Derived from Two Components with Alkane Chains of Different Lengths"					
12. PERSONAL AUTHOR(S) J.P. Folkers, P.E. Laibinis, and G.M. Whitesides					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) July 1992	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This paper describes the preparation and wetting properties of two-component self-assembled monolayers (SAMs) obtained by the competitive adsorption of one short-chain (HS(CH ₂) ₁₀ Sh) and one long-chain (HS(CH ₂) ₂₁ Lg) alkanethiol onto gold from dilute ethanolic solutions. The four possible combinations of the tail groups CH ₃ and CH ₂ OH were investigated: Sh = CH ₃ /Lg = CH ₂ OH,					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Harold Guard			22b. TELEPHONE (Include Area Code) 202/696-4409		22c. OFFICE SYMBOL

$\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_3$, $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_2\text{OH}$, and $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_3$.

The compositions of these SAMs are not the same as the compositions of the solutions from which they were formed, and the relationship between these compositions suggests that the SAMs have partially phase separated. Contact angles with water and hexadecane, however, show that significant disorder still remains in the interfacial region.

**Self-Assembled Monolayers of Alkanethiols on Gold:
Monolayers Derived from Two Components with Alkane Chains
of Different Lengths.**

John P. Folkers, Paul E. Laibinis, and George M. Whitesides*

Department of Chemistry
Harvard University
Cambridge MA, 02138

DTIC QUALITY INSPECTED 3

Abstract

This paper describes the preparation and wetting properties of two-component self-assembled monolayers (SAMs) obtained by the competitive adsorption of one short-chain ($\text{HS}(\text{CH}_2)_{10}\text{Sh}$) and one long-chain ($\text{HS}(\text{CH}_2)_{21}\text{Lg}$) alkanethiol onto gold from dilute ethanolic solutions. The four possible combinations of the tail groups CH_3 and CH_2OH were investigated: $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_2\text{OH}$, $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_3$, $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_2\text{OH}$, and $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_3$. The compositions of these SAMs are not the same as the compositions of the solutions from which they were formed, and the relationship between these compositions suggests that the SAMs have partially phase separated. Contact angles with water and hexadecane, however, show that significant disorder still remains in the interfacial region.

Accession For	
NTIS	CRA&I ☒
DTIC	TAB ☐
Unannounced ☐	
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

1. Introduction

In this paper, we describe the adsorption and wetting properties of two-component self-assembled monolayers (SAMs) prepared by the adsorption of alkanethiols with different lengths of alkyl chains -- $\text{HS}(\text{CH}_2)_{\text{sh}}\text{Sh}$ and $\text{HS}(\text{CH}_2)_{\text{lg}}\text{Lg}$, where $\text{sh} = 10$ and $\text{lg} = 21$, and Sh and Lg are either CH_2OH or CH_3 -- onto freshly evaporated gold substrates. We have studied the four possible combinations of Sh and Lg ($\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_3$, $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_2\text{OH}$, $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_3$, and $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_2\text{OH}$). We have described some of the details of these systems previously [1-2]; in this paper, we focus on the composition of the SAM: its dependence on the conditions for adsorption, and its effect on the wetting properties. We will introduce this work with a brief overview of the area of SAMs of alkanethiols on gold. We then discuss the relationship between the composition of the SAM and the composition of the solution. In the final section, we describe some of the wetting properties of these two-component SAMs, concentrating on the relationship between wettability and the composition of the SAM.

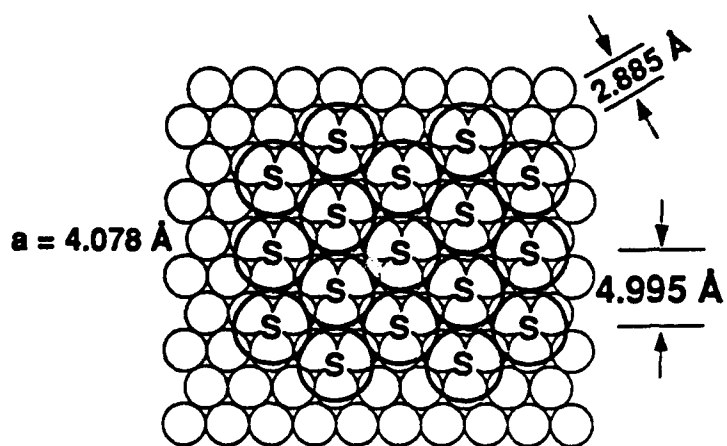
2. Background

Among the many systems currently available for the formation of self-assembled monolayers [3-14], SAMs obtained by the adsorption of alkanethiols ($\text{HS}(\text{CH}_2)_n\text{X}$) onto gold (and, perhaps, onto silver [11,12]) are the most versatile: the strength and specificity of the metal-sulfur interaction allows the introduction of many important terminal functional groups (X) into

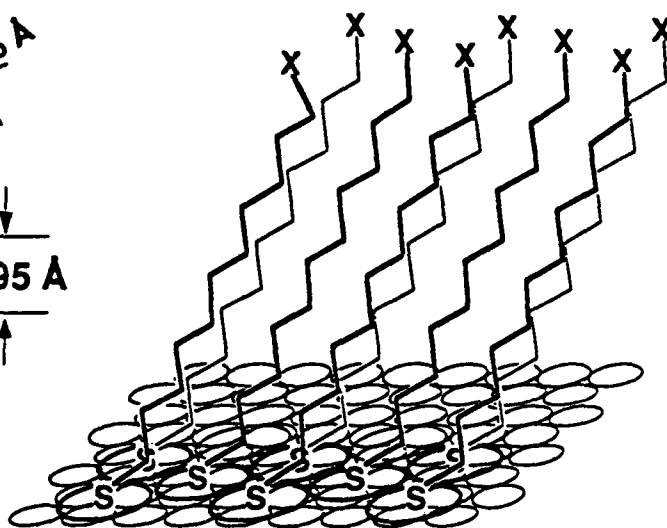
the monolayers [10,15-21]. The highly ordered structure of these SAMs has been established using a variety of techniques, including polarized infrared external reflectance spectroscopy (PIERS) [9,11,12,15,22], electron diffraction [23], helium scattering [24,25], X-ray scattering [25,26], scanning tunneling microscopy [27], and surface Raman spectroscopy [28] (Figure 1); these techniques yield a structure in agreement with molecular dynamics calculations [29]. This structure exposes the terminal functional groups (X) at the monolayer-air interface, and thus allows the interfacial properties of the monolayer to be controlled by changing X. Model systems based on these SAMs have become increasingly important in fundamental studies of electrochemistry [19,30], protein adsorption [20], X-ray induced damage to organic materials [31], and wetting [1,2,10,13,16-18,20,32-35].

Our interest in these SAMs is based in an interest in the physical-organic chemistry of organic interfaces, especially the relationships between molecular structure and wetting [1,2,13,16-18,20,34]. SAMs derived from the adsorption of alkanethiols onto gold provide a molecular basis for studies of wettability. In our investigations of the wettability of SAMs, we have utilized two approaches: formation of single-component SAMs with terminal functional groups of variable hydrophilicity [10,13,16-18,20], and formation of two-component SAMs [1,2,13,16,18,20]. The latter method provides the greater degree of control over the properties of the interface, because the relative concentrations of the two components in the SAM can be adjusted. In this study, we have examined the effect of disorder

Figure 1. The structure of alkanethiolates adsorbed on gold (111). Thiulates are adsorbed at three-fold hollows on the surface forming a commensurate $\sqrt{3}\times\sqrt{3}$ R30° structure [23-26]. The alkyl chains are in a trans zig-zag array (the small concentration of gauche conformers is localized near the ends of the chains [12,24,29]), and are oriented about 30° from the surface normal [9,12,16,22]. Because of this highly ordered structure, the tail groups (X) are localized at the monolayer-air interface.



Au (111) • AuSR
 $\sqrt{3} \times \sqrt{3} \text{ R } 30^\circ$

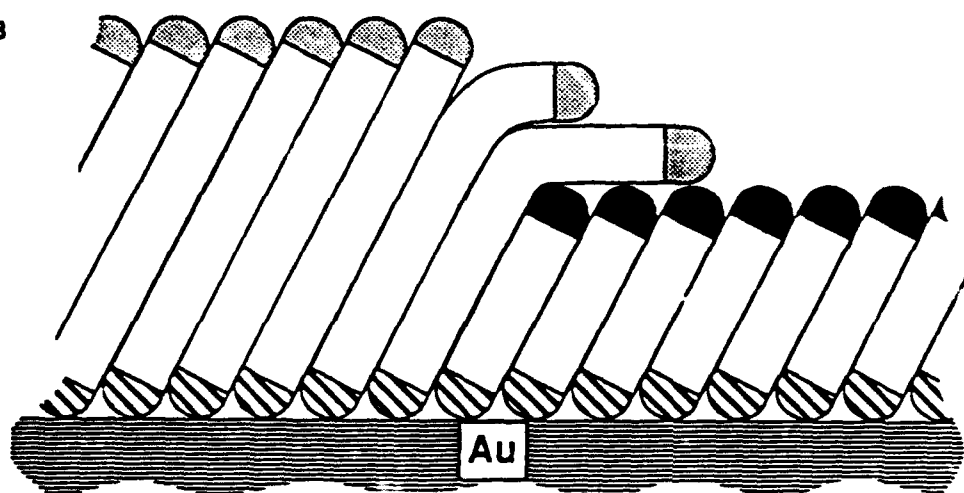
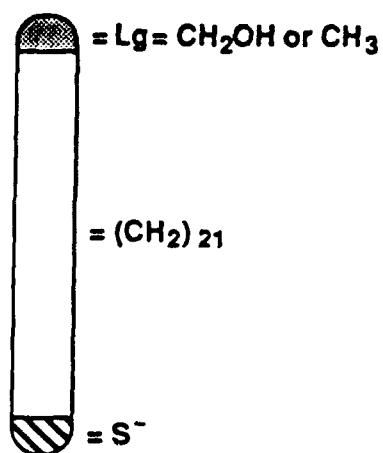
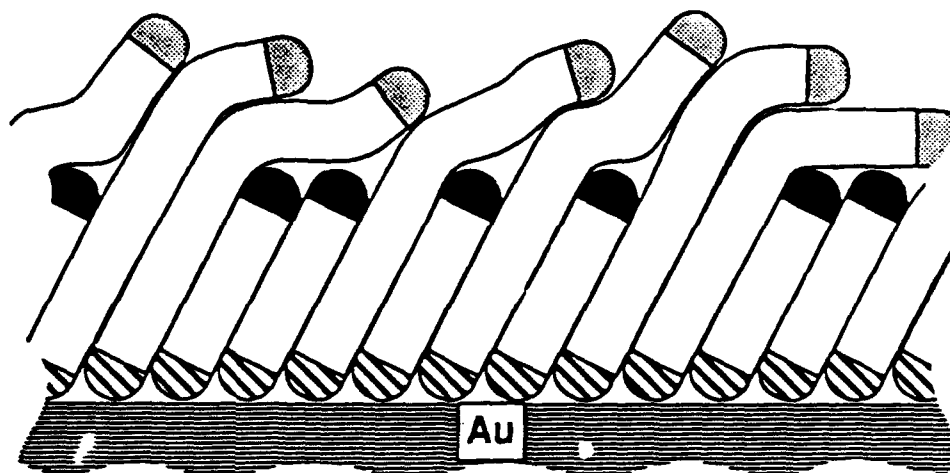
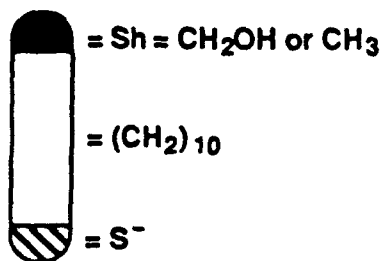


in the interfacial region on the wettability of two-component ("mixed") SAMs by adjusting the relative concentrations of two alkanethiolates with different lengths [1,2,13].

In mixed SAMs containing one long-chain component and one short-chain component, the region close to the gold substrate that is occupied jointly by the short chains and the corresponding sections of the long chains is well-ordered; the region further away from the gold that is occupied only by the remainder of the long chains is disordered (as long as the components have not phase separated; see Figure 2) [36]. The results reported in this paper indicate that, under conditions commonly used in forming mixed SAMs, there appears to be some phase separation of the two components in the SAM, but enough disorder remains to affect the contact angles [1,2].

We have chosen $sh = 10$ and $lg = 21$ in our work; these classes of thiols are synthetically accessible and soluble in ethanol at millimolar concentrations [1,2]. We can easily determine the compositions of SAMs containing mixtures of these long and short thiolates by several techniques [2]. X-ray photoelectron spectroscopy (XPS) is the most useful single technique: XPS provides elemental composition and oxidation states in addition to the relative concentrations of the two components in the SAMs. In this paper, we have used the natural logarithm of the ratio of the carbon 1s intensity to the gold 4f intensity (i.e. $\ln [C(1s)/Au(4f)]$) to determine the compositions of the SAMs [2]. Our group has shown previously that this quantity can be used to determine the compositions of SAMs incorporating thiolates of

Figure 2. Schematic representation of a mixed SAM of a long-chain and short-chain component with $R_{SAM} = 1$ ($\chi_{Lg, SAM} = 0.5$). The top drawing shows a monolayer with the components randomly mixed, and the bottom shows the two components phase separated. We believe that our SAMs are somewhere between these two extremes.



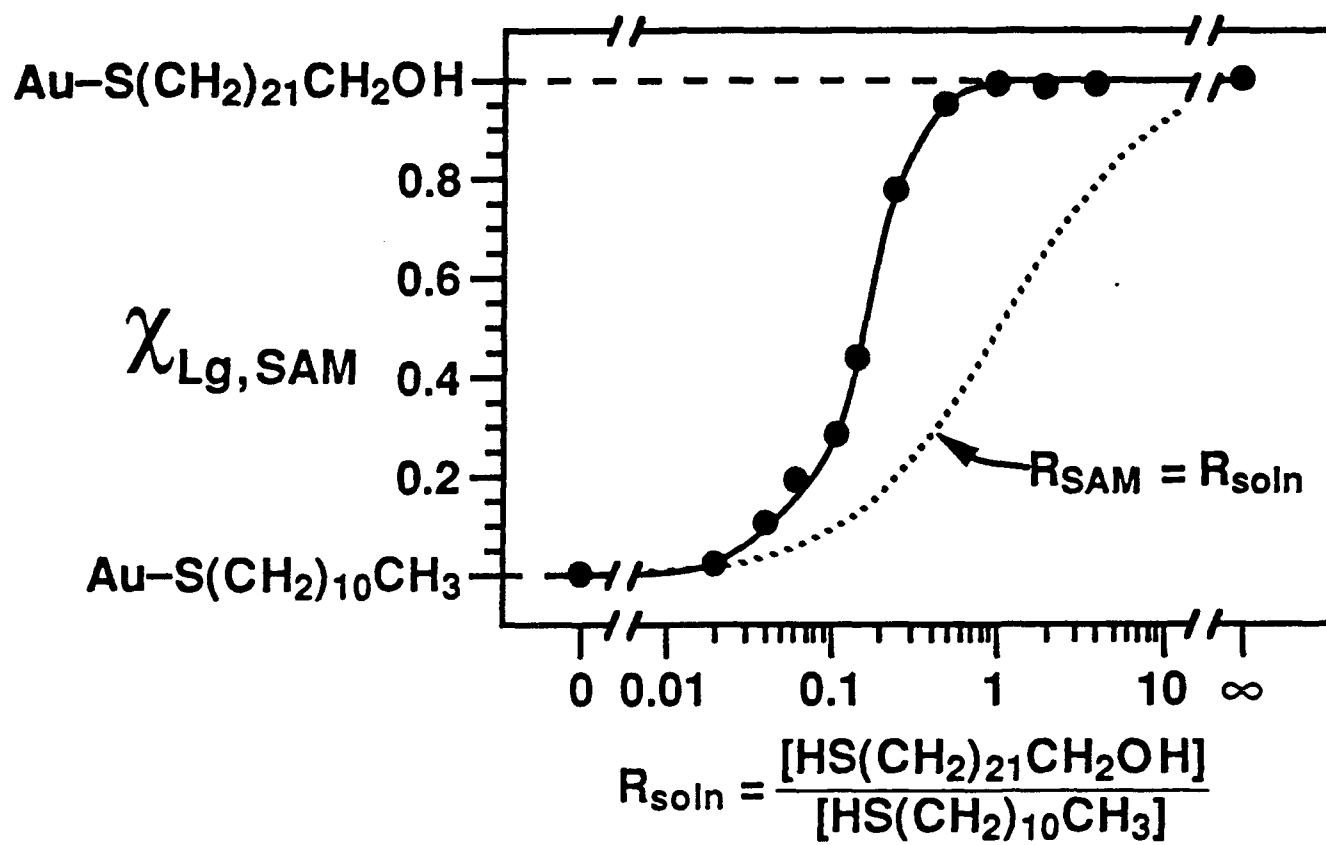
different lengths [1,37]. This method is excellent for characterizing the compositions of a group of mixed SAMs because it minimizes error due to drift in the intensity of the X-ray source.

The work described here is focused on the tail groups methyl and hydroxymethyl; these groups provide a large difference in the wettabilities of the single-component SAMs, and a large range of wettabilities for the mixed SAMs [1,2,10]. The oxygen of the hydroxymethyl group also provides a "tag" for monitoring composition by XPS [2].

3. The Relationship between the Composition of the Solution and the Composition of the SAM.¹

When two-component SAMs are formed from thiols of different lengths under "normal adsorption conditions" (gold-coated silicon substrates immersed in ethanolic solutions containing a total concentration of thiol of 1 mM; one day; room temperature), the ratio of the concentrations of the two thiolates in the SAM ($R_{SAM} = [Au(I)^-S(CH_2)_{1g}Lg]/[Au(I)^-S(CH_2)_{sh}Sh]$) and the ratio of concentrations of the respective thiols in solution ($R_{soln} = [HS(CH_2)_{1g}Lg]/[HS(CH_2)_{sh}Sh]$) are not the same (Figure 3). In Figure 3, we have plotted the compositions of the SAMs as the mole fraction of the longer component ($\chi_{Lg,SAM}$, where $\chi_{Lg,SAM} = [Lg]_{SAM}/([Lg]_{SAM} + [Sh]_{SAM})$ and $\chi_{Lg,SAM} + \chi_{Sh,SAM} = 1$) [1,2]. The deviation from ideality ($R_{SAM} = R_{soln}$; dashed line in Figure 3) indicates a preference of the longer component for the surface,

Figure 3. Comparison of compositions of SAMs and of the solutions from which they were formed: mixed SAMs formed from the competitive adsorption of $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ (ethanolic solutions with total concentration of thiol of 1 mM; room temperature; one day). The x-axis is R_{soln} , defined as the ratio of the concentrations of the longer component and the shorter component in solution. The y-axis is the mole fraction of the longer component in the SAM ($\chi_{\text{Lg},\text{SAM}}$, where $\chi_{\text{Lg},\text{SAM}} + \chi_{\text{Sh},\text{SAM}} = 1$), determined from the logarithm of the ratio of intensity of the carbon (1s) peak in XPS to that of the gold (4f) peak [37]. Some data points may have $\chi_{\text{Lg},\text{SAM}} < 0$ or $\chi_{\text{Lg},\text{SAM}} > 1$ because of errors in the measurements: If the intensities of both the carbon (1s) signal and the gold (4f) signal vary by about $\pm 5\%$, then values of $\ln(\text{C}/\text{Au})$ vary by $\pm 7\%$, resulting in a minimum error of $\pm 7\%$ in the values of $\chi_{\text{Lg},\text{SAM}}$. We have left these data points outside $\chi_{\text{Lg},\text{SAM}} = 0$ and $\chi_{\text{Lg},\text{SAM}} = 1$ (rather than moving them to the endpoints) to show the error in the measurements. The curve through the data is only a guide to the eye. The dashed curve represents $R_{\text{SAM}} = R_{\text{soln}}$.

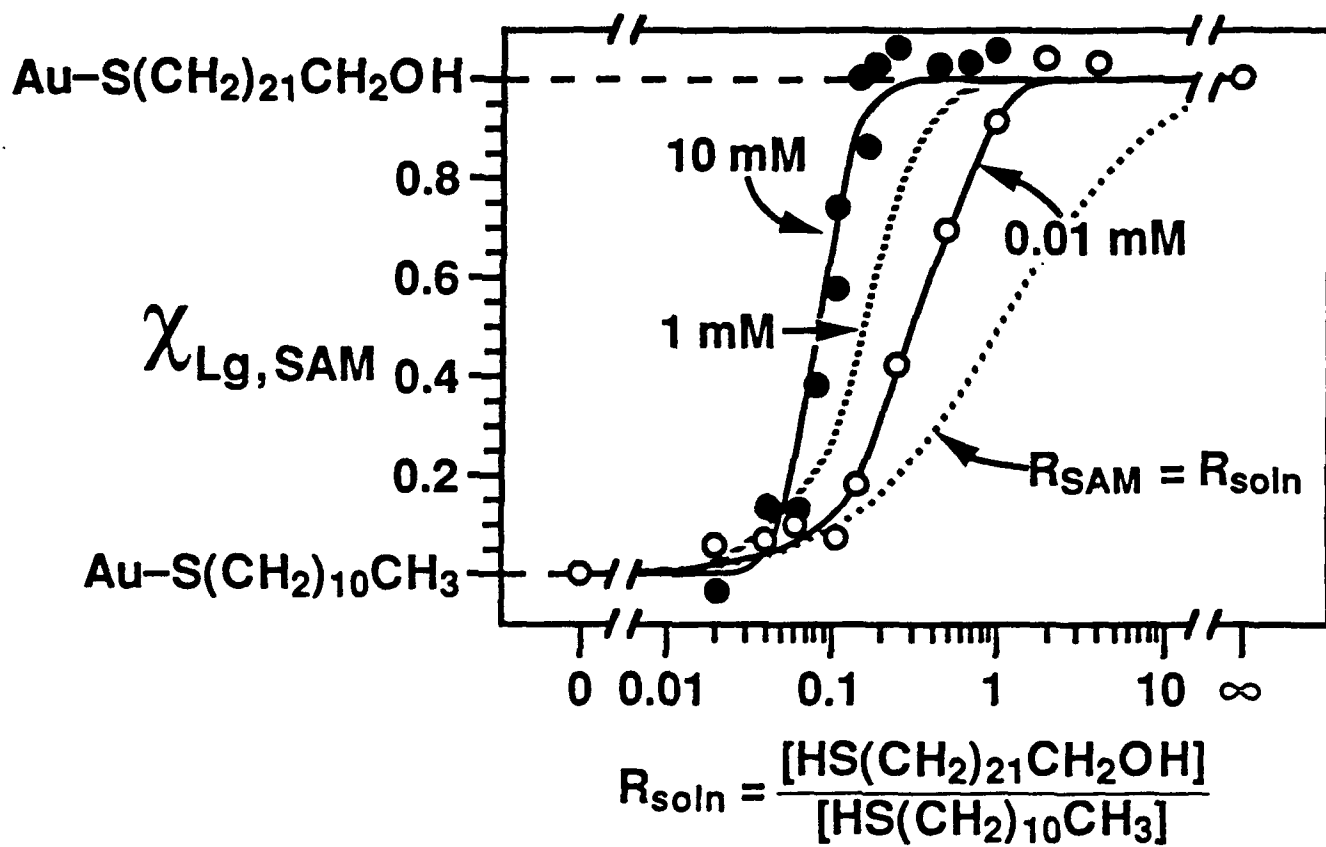


and also suggests partial phase separation of the two components in the SAM.

We have inferred partial phase separation of these components from the observed relationship between the composition of the SAM and the composition of the solution [1,2]. When $R_{\text{soln}} > \sim 0.8$ ($\chi_{\text{Lg,soln}} > \sim 0.44$) for $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_2\text{OH}$ (Figure 3), the SAM is comprised almost exclusively of the longer component ($\chi_{\text{Lg,SAM}} = 1$); when $R_{\text{soln}} < \sim 0.02$, the SAM is comprised almost exclusively of the shorter component ($\chi_{\text{Lg,SAM}} = 0$). Mixed SAMs are therefore only formed in a limited region of R_{soln} : this observation suggests that the two components do not mix well within the SAM. The sharpness and position of the transition region relative to $R_{\text{SAM}} = R_{\text{soln}}$ suggests the following qualitative energy ranking for interactions within the SAM: $\text{Lg} \cdot \text{Lg} > \text{Sh} \cdot \text{Sh} > \text{Lg} \cdot \text{Sh}$. We cannot, however, determine absolute energies for these interactions because these systems are not at equilibrium.

Even though we do not know the detailed molecular mechanism of formation of SAMs, or the mechanism(s) of exchange between thiolates on the surface and thiols in solution [39], we know that these SAMs are not at equilibrium: the relationship between the composition of the SAM and the composition of the solution is not stable to changes in the conditions used for adsorption. For example, increasing the total concentration of thiol in solution resulted in an increase in the preference for the longer component in the SAM, and also an increase in the extent of apparent phase separation (i.e. the transition region sharpens; Figure 4); the opposite effect occurred when the total concentration of thiol was

Figure 4. Comparison of compositions of SAMs and of the solutions from which they were formed: The effect of changing the total concentration of thiol in solution. Filled circles: Mixed SAMs formed from the competitive adsorption of $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ from ethanolic solutions with total concentrations of thiol of 10 mM at room temperature for one day. Open circles: Mixed SAMs formed from the competitive adsorption of $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ from ethanolic solutions with total concentrations of thiol of 0.01 mM at room temperature for one day. Axis labels are described in the caption to Figure 3. The curves through the data are only guides to the eye. The dashed curve between the two sets of data represents the curve through the data in Figure 3; the dashed curve on the right represents $R_{\text{SAM}} = R_{\text{soln}}$.



decreased (Figure 4). The effect of increasing the time for adsorption was similar to raising the total concentration of thiol in solution [38]. In some cases, increasing the temperature of the solution also affected the relationship between the composition of the solution and the composition of the SAM in a manner suggesting that SAMs formed under normal conditions are not at equilibrium: For $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_3$, the transition region became nearly an abrupt step when the temperature of the solutions was raised from 25 °C to 60 °C [38]. From these changes,ⁱⁱ we conclude that the SAMs are not in thermodynamic equilibrium: exchange between species in solution and species in the completed SAM is slow at room temperature.

We emphasize here that these results may be a function of the crystallinity and morphology of our gold substrates. These substrates -- formed by electron-beam evaporation of 2000 Å of gold at room temperature onto chromium-primed silicon wafers -- are rough on the atomic scale: they consist of crystallites of gold that have widths of approximately 100 nm and heights of 20-30 nm, as determined using scanning tunneling microscopy [2]. If we were to use gold substrates with large, atomically smooth terraces [40], we might observe a different relationship between R_{SAM} and R_{soln} .

4. The Relationship between Wettability and the Composition of the SAM [1,2].

We have used water and hexadecane as our probe liquids because of the large difference in their surface tensions

($\gamma_{LV}^{H_2O} = 73$ dyn/cm; $\gamma_{LV}^{HD} = 28$ dyn/cm at room temperature [41]) and in the origins of the forces that determine them. Approximately 70 % of the surface tension of water originates in its polar interactions, predominantly hydrogen bonding [42]; wetting by water is, therefore, strongly affected by changes in the polarity of the interface. The surface tension of hexadecane has no polar component; in the absence of any polar functionality, hexadecane is sensitive primarily to changes in the polarizability of the groups at the interface. In this section, we first discuss the contact angle of water on the set of SAMs we have studied. We follow with a discussion of contact angles involving hexadecane on mixed SAMs without polar groups (i.e. $Sh = CH_3/Lg = CH_3$). We conclude with an incomplete discussion of hysteresis in the contact angle of water on these SAMs. Hysteresis is still incompletely understood [43,44], but has the potential to provide substantial useful information about the heterogeneity of surfaces.

All of the contact angles discussed in this section were taken on SAMs formed under normal adsorption conditions. To the present, we have not observed any general trends in the contact angles as a function of the conditions used for adsorption [38]. In this work, we have taken maximum advancing (θ_a) and minimum receding (θ_r) contact angles [10,44]. In presenting our data, we plot the cosine of the contact angle as in Young's equation [45]: $\cos \theta = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$, where the γ_{XY} refers to the interfacial free energy per unit area between interfaces X and Y (S = Solid, L = Liquid, V = Vapor).

(1) *Wettability with Water.* When only one of the tail groups is hydroxymethyl (i.e. $Sh = CH_3/Lg = CH_2OH$ or $Sh = CH_2OH/Lg = CH_3$), the wettabilities of the mixed SAMs span the range between hydrophobic and hydrophilic. Since R_{SAM} is not simply related to R_{soln} , no correlation exists between the wettability of the SAM and the composition of the solution (Figure 5 bottom). In this system ($Sh = CH_3/Lg = CH_2OH$), both the advancing and receding contact angles are, however, linearly related to the composition of the SAM (i.e. $\chi_{Lg,SAM}$; Figure 5 top). These data might suggest that the contact angles are not affected by disorder in the interfacial region or that the mixed SAMs are not disordered, but since methylene groups are as hydrophobic as methyl groups (see below), using water as a probe liquid, we cannot reliably differentiate between a SAM that has phase separated into macroscopic islands and a SAM with randomly dispersed hydroxymethyl groups in a sea of methyl and methylene groups.

For $Sh = CH_2OH/Lg = CH_3$, only the receding contact angles of water are linearly related to the composition of the SAM; the plot of advancing contact angle of water against $\chi_{Lg,SAM}$ is curved (Figure 6). These data illustrate the high sensitivity of the contact angles to the molecular structure of the interface: If this system were macroscopically phase separated, we would expect that the advancing angles would be related linearly in the composition of the SAM. This result implies significant disorder at the interface: the longer chains are flopping over the shorter chains while the drop of water is advancing, but while the drop is

Figure 5. Advancing (filled circles) and receding (open circles) contact angles of water on mixed SAMs obtained by the adsorption of $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ onto gold as a function of mole fraction of the longer component in the SAM, $\chi_{\text{Lg,SAM}}$ (top), and as a function of the mole fraction of the longer component in solution, $\chi_{\text{Lg,soln}}$ (bottom). Values of $\chi_{\text{Lg,SAM}}$ were determined as described in the caption to Figure 3; $\chi_{\text{Lg,soln}} = R_{\text{soln}}/(1 + R_{\text{soln}})$. Straight lines through the data in the top plot were determined by a least-squares fit. The curves through the data in the bottom plot are only guides to the eye.

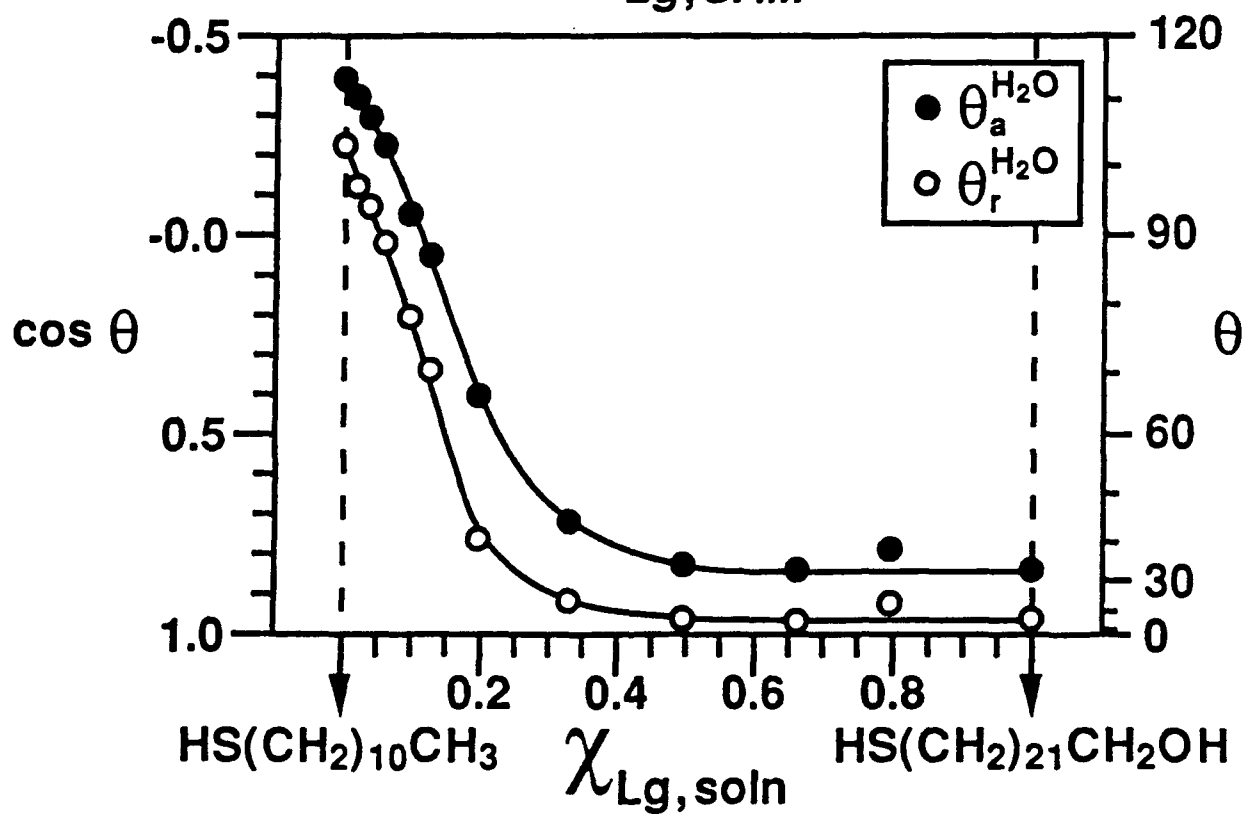
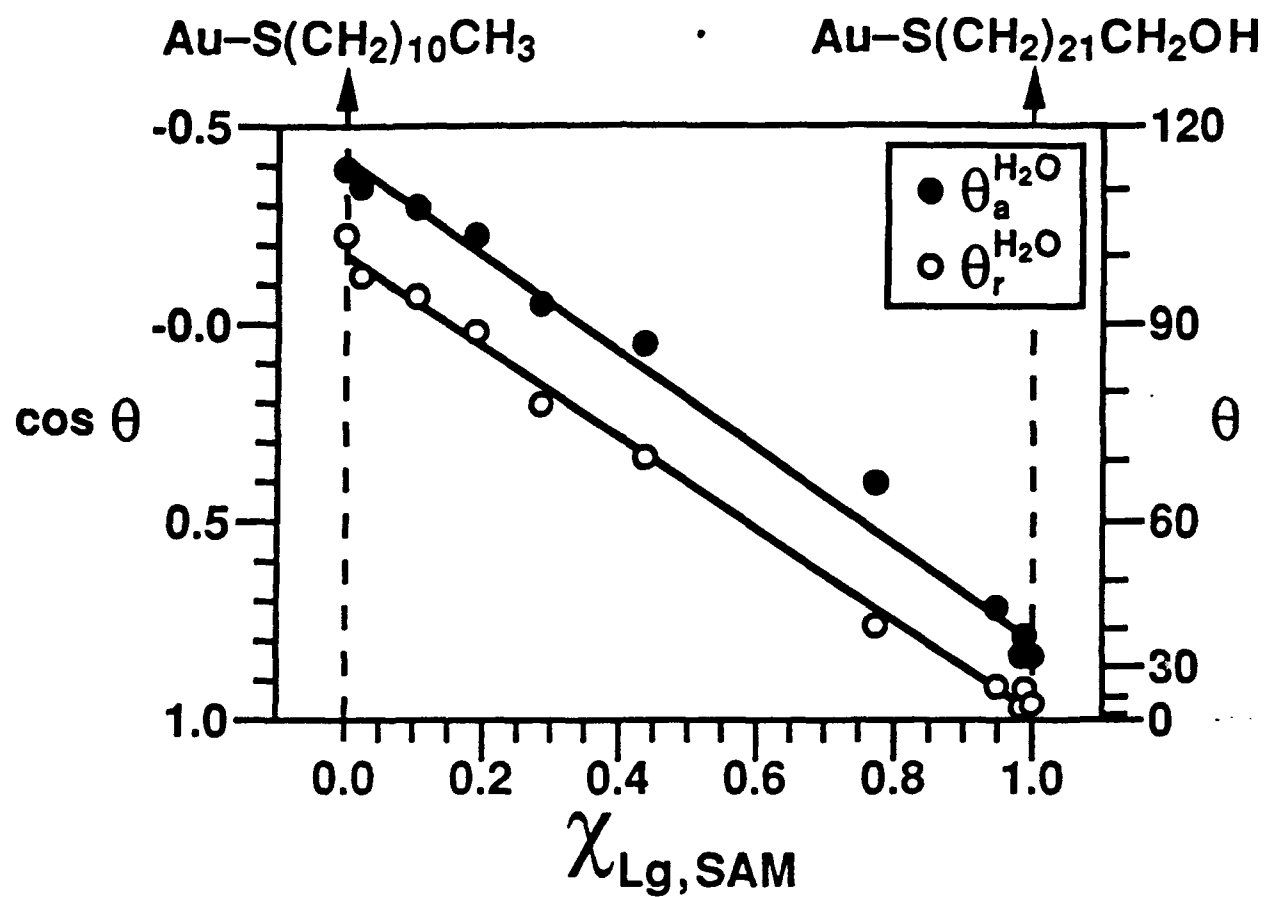
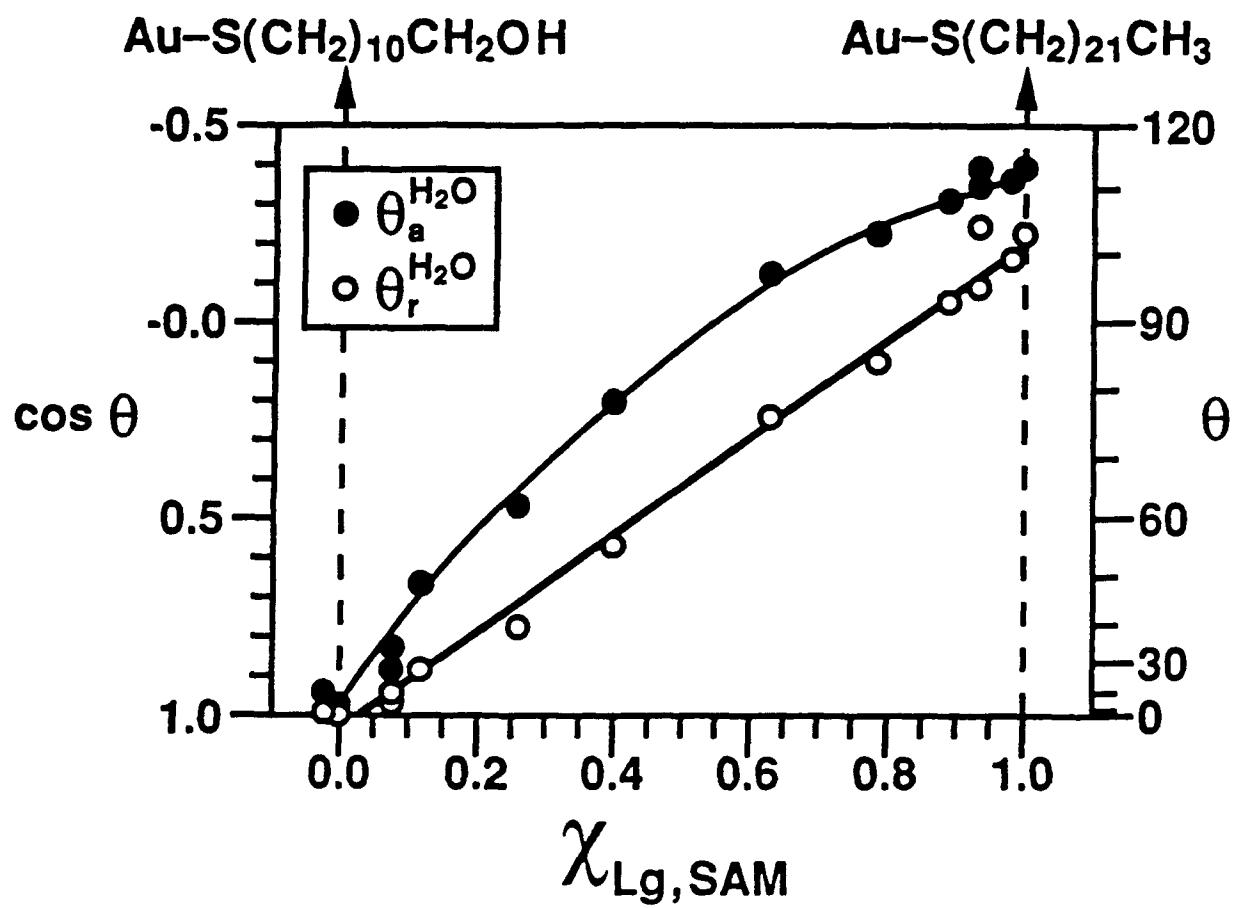


Figure 6. Advancing (filled circles) and receding (open circles) contact angles of water on mixed SAMs obtained by the adsorption of $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ onto gold as a function of the mole fraction of the longer component in the SAM. The mole fractions were determined as described in the caption to Figure 3. The straight line through the receding angles were determined by a least-squares fit. The curve through the data of the advancing contact angles is only a guide to the eye.



receding, the SAM could reorganize to uncover the hydroxymethyl groups.

When both tail groups are hydroxymethyl (i.e. $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_2\text{OH}$), the mixed SAMs are considerably more hydrophobic than the single-component SAMs (Figure 7). The advancing contact angle increases from about 20° for the pure SAMs to 54° for the SAM with $\chi_{\text{Lg,SAM}} = 0.5$. This change corresponds to a decrease in the interfacial free energy of the system ($\gamma_{\text{SV}} - \gamma_{\text{SL}}$) of ~ 25 dyn/cm (or ~ 0.8 kcal/mol of surface groups, assuming a constant concentration of surface groups $= 8 \times 10^{-10}$ moles/cm² [23,24,27]). We have observed previously that the advancing contact angle of water on mixed SAMs derived from $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{18}\text{CH}_2\text{OH}$ increased to 41° from $\sim 10^\circ$ on the single component SAMs ($\gamma_{\text{SV}} - \gamma_{\text{SL}}$ decreases by 17 dyn/cm or 0.5 kcal/mol) [1].iii For the contact angle to increase on these mixed SAMs, there must be significant interaction between the probe liquid and the methylene groups of the longer chains. The results observed imply significant disorder at the monolayer-water and monolayer-vapor interfaces. We cannot, however, interpret the changes in contact angle on this set of SAMs in terms of a model for the mixing of the components.

Mixed phases of $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_3$ are as hydrophobic (as determined by the advancing contact angle of water) as the highly ordered, single-component SAMs (Figure 8). While the contact angles of hexadecane clearly show that the interface is disordered (see Figure 9), the advancing contact angle of water is unaffected by the presence of methylene groups at the interface. Generally,

Figure 7. Advancing (filled circles) and receding (open circles) contact angles of water on mixed SAMs obtained by the adsorption of $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_2\text{OH}$ onto gold as a function of the mole fraction of the longer component in the SAM. The mole fractions were determined as described in the caption to Figure 3. The curves through the data are only guides to the eye.

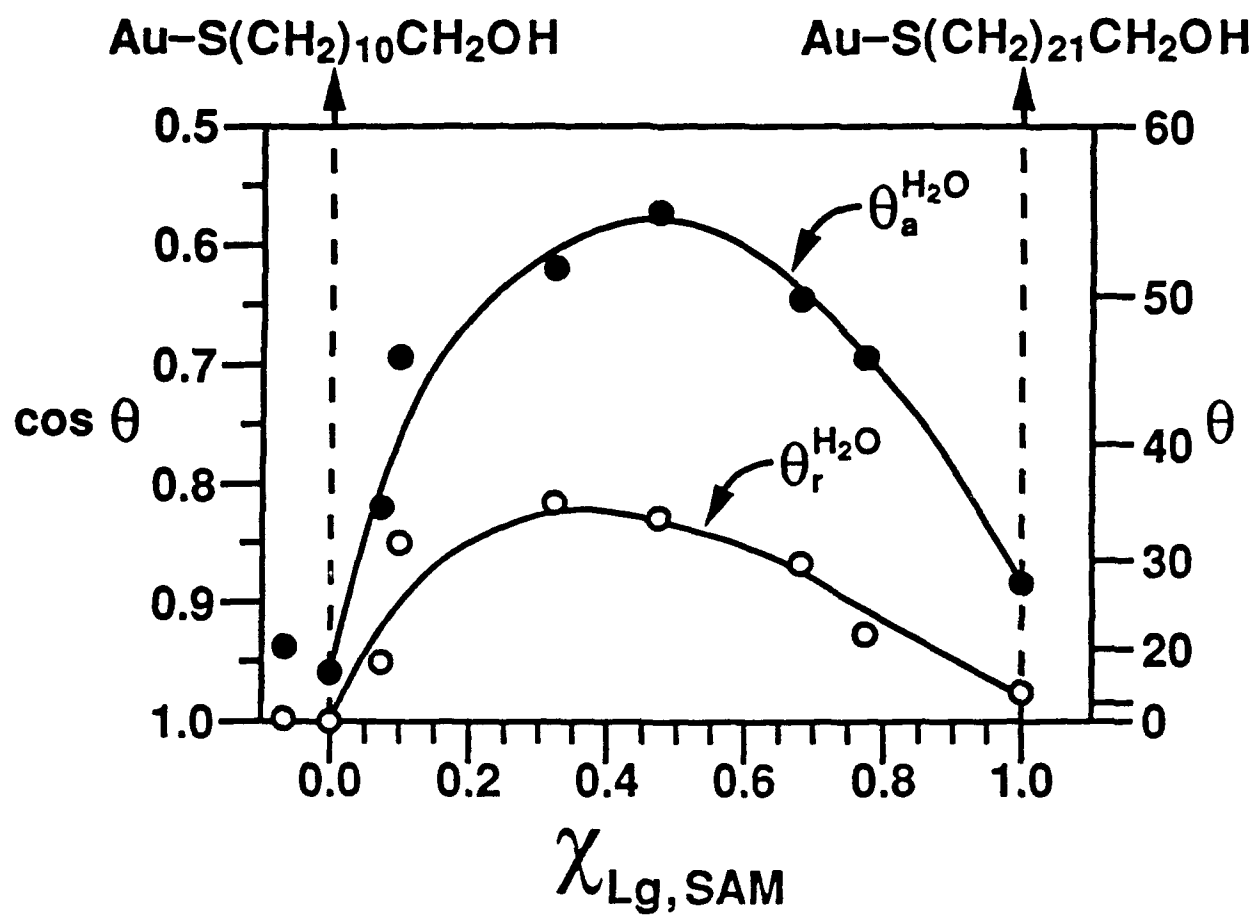
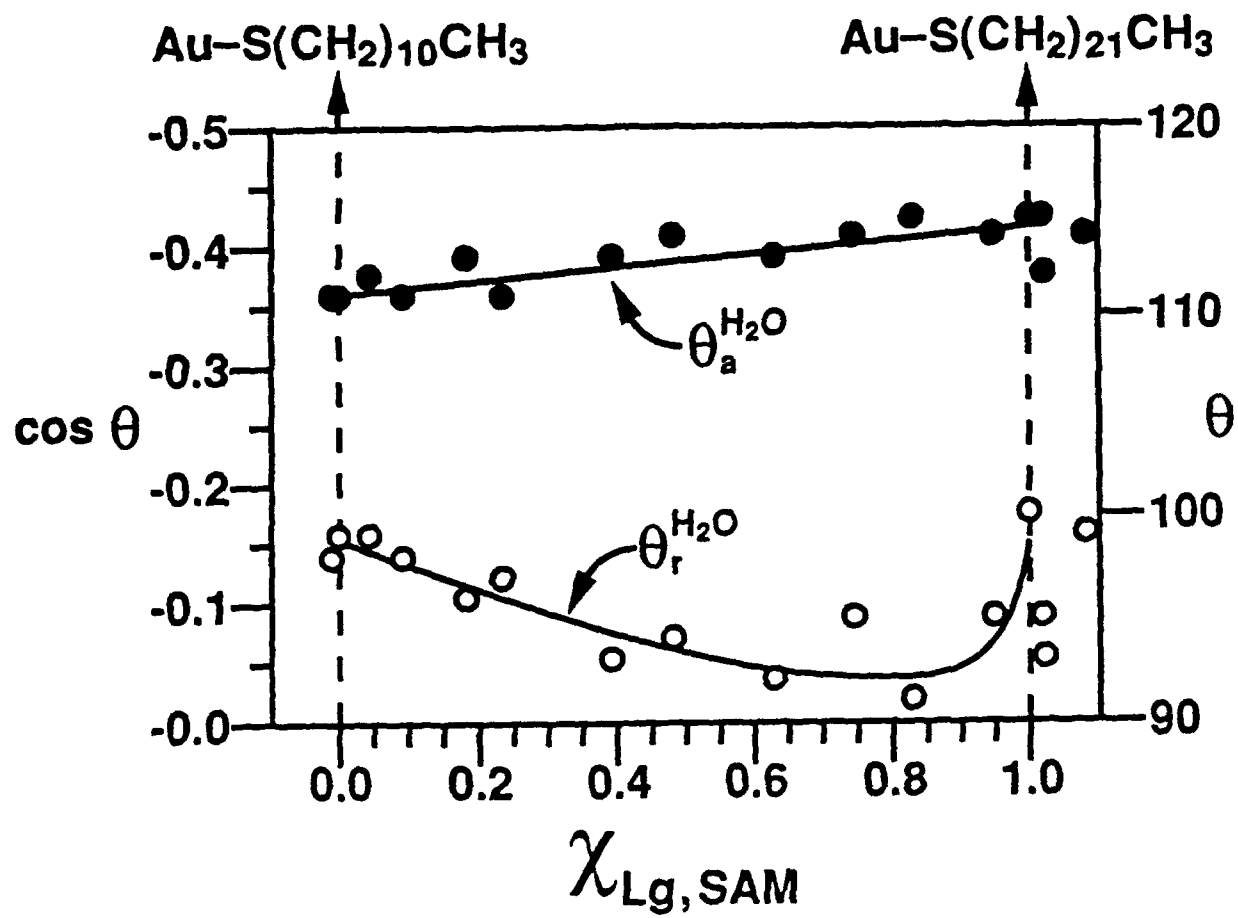


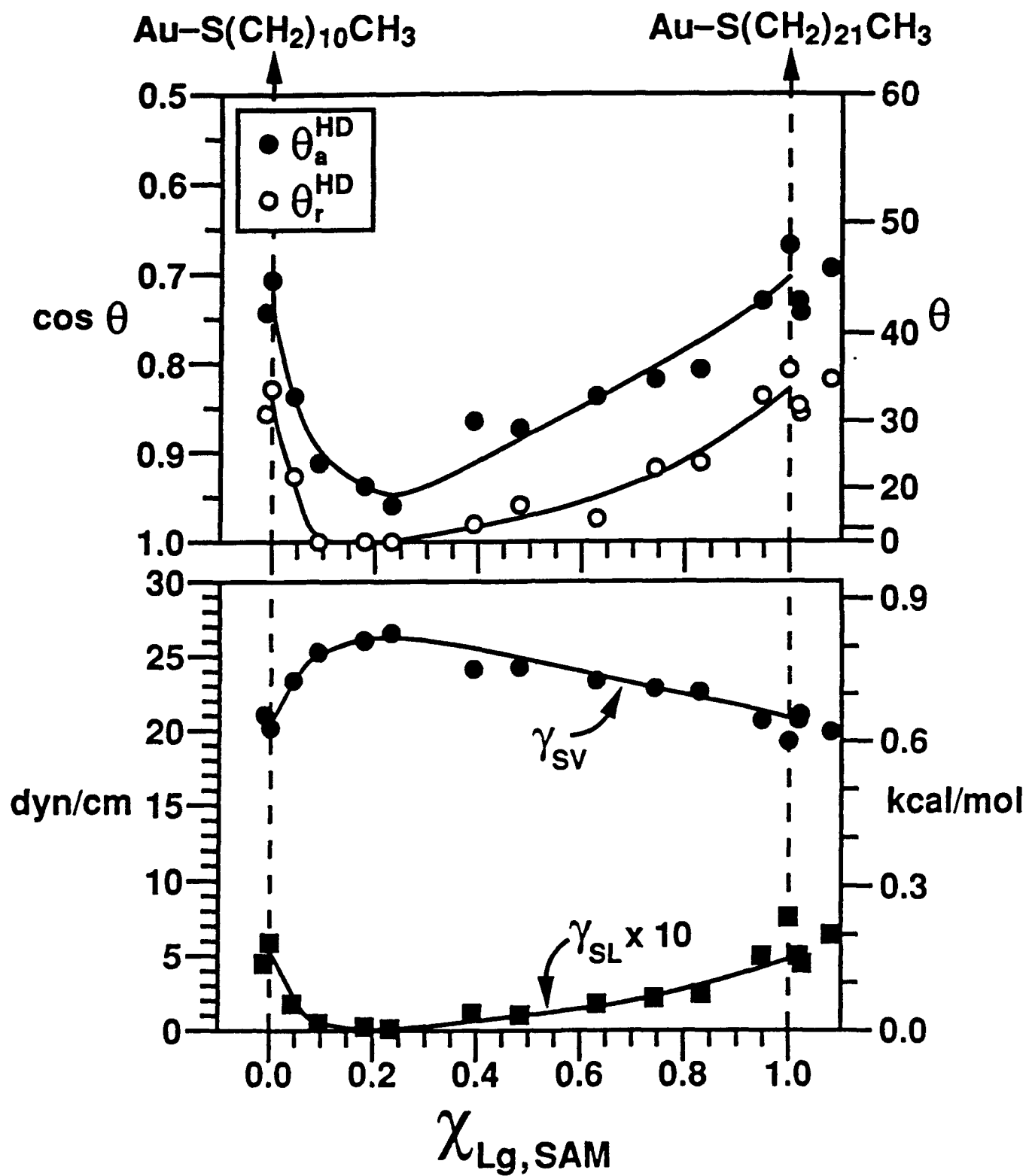
Figure 8. Advancing (filled circles) and receding (open circles) contact angles of water on mixed SAMs obtained by the adsorption of $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ onto gold as a function of the mole fraction of the longer component in the SAM. The mole fractions were determined as described in the caption to Figure 3. The curves through the data are only guides to the eye.



a surface composed of methyl groups has a γ_{sv} of about 20 dyn/cm, and one of methylene groups, $\gamma_{sv} = 30$ dyn/cm (e.g. polyethylene) [47]; this difference should lead to a decrease in the equilibrium contact angle of water by $\sim 8^\circ$ using Fowkes' equation for non-polar surfaces: $\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_{sv}\gamma_{lv}^d}$, where the superscript d refers to the dispersive component of the surface tension of the liquid ($\gamma_{lv}^d = 51$ dyn/cm for water at room temperature) [48]. The receding contact angle of water decreased on the mixed phases by about 8° suggesting that the equilibrium contact angle of water probably also decreased; this result is consistent with the introduction of some methylene groups at the interface. In a system with the ability to reorganize such as SAMs, these results (and those for $Sh = CH_2OH/Lg = CH_3$) might imply that the system minimizes γ_{sv} during the measurement of the advancing contact angle of water, and minimizes γ_{sl} during the measurement of the receding contact angle of water.

(2) *Wettability with Hexadecane.* The most interesting details about disorder in these SAMs that can be inferred from the contact angle of hexadecane were obtained on $Lg = CH_3/Sh = CH_3$. When the two methyl-terminated components were mixed on the surface, the advancing contact angle of hexadecane decreased from $\sim 45^\circ$ on the single-component SAMs to 16° (Figure 9) on the mixed SAM with $\chi_{Lg,SAM} = 0.2$. If we assume that this decrease is analogous to the decrease in the equilibrium contact angle, we can use Fowkes' equation [48] to determine the solid-vapor and solid-liquid interfacial tensions of these SAMs (Figure 9 bottom). The maximum decrease in the advancing contact angle of hexadecane from

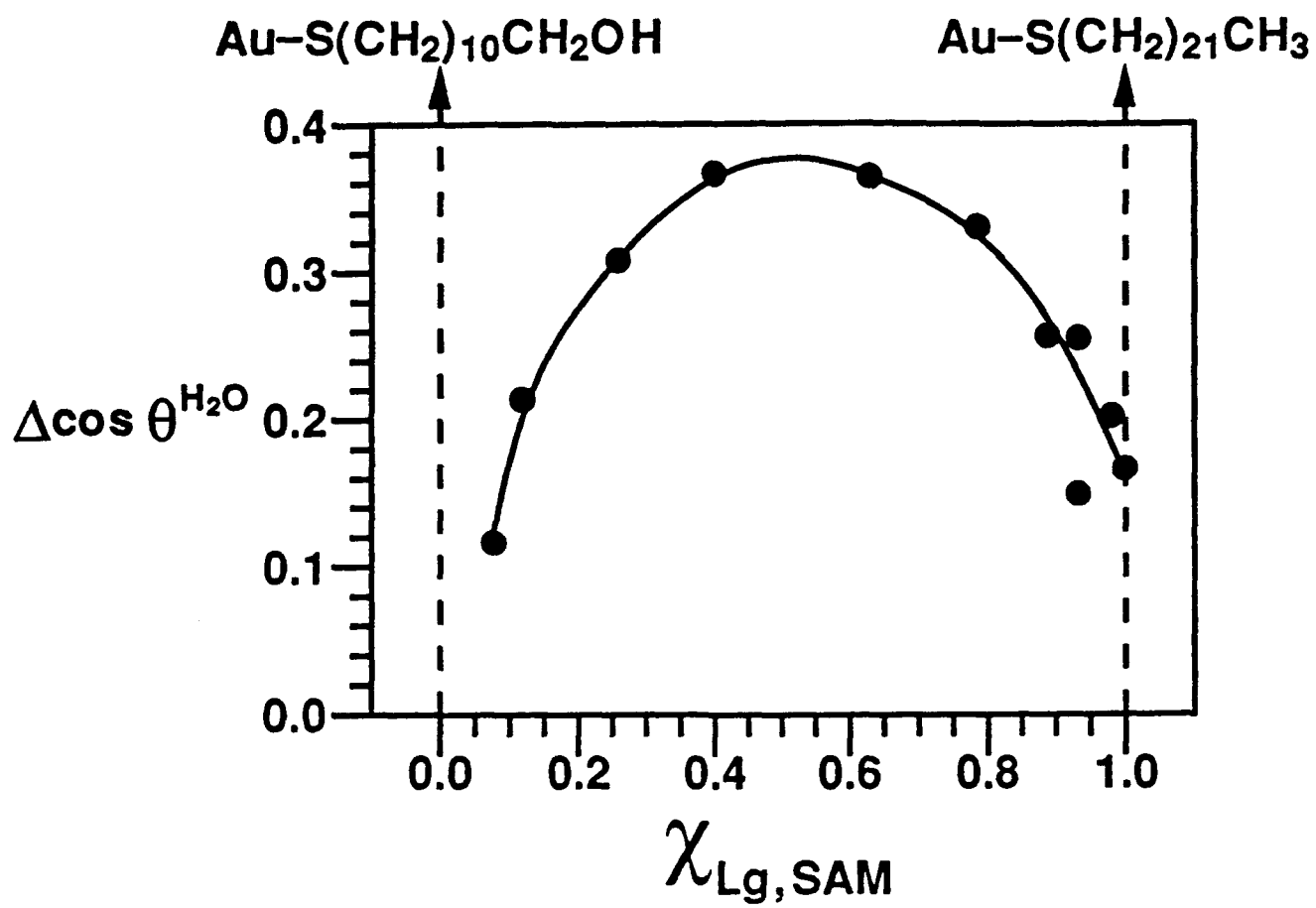
Figure 9. Top: Advancing (filled circles) and receding (open circles) contact angles of hexadecane on mixed SAMs obtained by the adsorption of $\text{HS}(\text{CH}_2)_{10}\text{CH}_3$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ onto gold as a function of the mole fraction of the longer component in the SAM. Bottom: Solid-vapor (γ_{SV} ; filled circles) and solid-liquid (γ_{SL} ; filled squares) interfacial tensions determined using the advancing contact angles of hexadecane and Fowkes' equation [48]. Values of γ_{SL} have been multiplied by ten to bring them on scale. The mole fractions were determined as described in the caption to Figure 3. The curves through the data are only guides to the eye.



the values on the single-component SAMs corresponds to an increase in γ_{SV} by about 6.5 dyn/cm (0.20 kcal/mol of surface groups), and a decrease in γ_{SL} by about 0.6 dyn/cm (0.02 kcal/mol of surface groups).^{iv} Obviously, disorder in this system leads to an increase in the numbers of methylene groups at the interface. While hexadecane is most sensitive to the methylene groups at $\chi_{Lg,SAM} = 0.2$, water is most sensitive to disorder between $\chi_{Lg,SAM} = 0.4$ and 0.8; we do not have an explanation for this difference in behavior.

(3) *Hysteresis in the Contact Angle of Water.* The hysteresis in the contact angle of water (defined here as $\Delta \cos \theta^{H_2O} = \cos \theta_r^{H_2O} - \cos \theta_a^{H_2O}$ to give positive values) increases in magnitude as the interface becomes more disordered. Figure 10 shows the hysteresis in the contact angle of water for the mixed SAMs of $Sh = CH_2OH/Lg = CH_3$ plotted against the composition of the SAM. The origin of this increase in hysteresis is probably the disorder in the interface, but we will not be able to quantify this effect until we can reproducibly control the roughness of our substrates and reduce the error in the measurement of the contact angles [2]. Theoretical and experimental studies of hysteresis have not addressed the problem of molecular-scale microheterogeneity at the interface [43,44], but once we understand the distribution of the two thiolates on the gold surface, SAMs derived from the types of components presented here will be a very useful tool for understanding fully the origins of hysteresis.

Figure 10. Hysteresis in the contact angle of water on mixed SAMs obtained by the adsorption of $\text{HS}(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ and $\text{HS}(\text{CH}_2)_{21}\text{CH}_3$ onto gold as a function of the mole fraction of the longer component on the surface. Values of hysteresis cannot be determined when the receding angle of water is zero, and therefore, there are no values of hysteresis below $\chi_{\text{Lg},\text{SAM}} \approx 0.1$. The curve through the data is only a guide to the eye.



5. Conclusions

The data summarized in this paper illustrate that two-component self-assembled monolayers of alkanethiolates on gold are important tools in understanding wetting. Contact angles using water and hexadecane are sensitive to disorder in the interfacial regions of mixed SAMs of alkanethiolates with alkyl chains of different lengths, but this sensitivity depends on the tail groups of the components and on the probe liquid: Water is sensitive to the increase in the concentration of methylene groups in the interfacial regions of mixed SAMs of $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_2\text{OH}$, but is only slightly sensitive to the increase in the concentration of methylene groups in the interfacial regions of mixed SAMs of $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_3$. Hexadecane is, however, very sensitive to changes in the relative concentrations of methyl and methylene groups in the interfacial region in mixed SAMs of $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_3$. Hysteresis on the contact angle of water increases on the mixed SAMs. This observation suggests that hysteresis is also sensitive to microscopic disorder in the interfacial region.

We do not believe that these SAMs are completely disordered: the relationship between the composition of the SAM and the composition of the solution suggests that these SAMs have partially phase separated under normal conditions for adsorption. We can change the degree of mixing of the two components in the plane of the monolayer by changing the conditions for adsorption, but we have yet to form a completely phase separated set of SAMs or a completely mixed set of SAMs. We are continuing to explore

the wetting and adsorption properties of these SAMs with the goals of determining and controlling the size of the islands in the SAM, and then relating the wetting properties (especially hysteresis) to the heterogeneity of the interfaces.

Acknowledgements

This research was supported in part by the Office of Naval Research, the Defense Advanced Research Projects Agency, and the National Science Foundation (Grant DMR-89-20490 to the Harvard University Materials Research Laboratory). J.P.F. acknowledges the National Institutes of Health for a training grant in biophysics (1989-1990). We would especially like to thank Colin Bain for initiating studies in this area.

Footnotes

- i) In this section, we have used the system $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_2\text{OH}$ to illustrate the relationship between composition of the SAMs and the composition of the solutions; the general trends are the same for the other systems we have studied [2,38].
- ii) We have not systemically addressed the influence of solvent on the character of two-component SAMs, but qualitative studies have suggested that the solvent has a large influence on the composition and structure of the SAM [1,16].
- iii) We commonly observe that the value of the advancing contact angle of water on hydroxymethyl-terminated monolayers quickly increases with the amount of time between removal of the sample from solution and the time that the contact angles are taken. We attribute this increase (which is relatively small in terms of $\cos \theta$) to airborne contaminants adsorbing to this high-energy surface, and not to reconstruction of the monolayer-air interface of the single-component SAMs [46].
- iv) The advancing contact angles of hexadecane on $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_2\text{OH}$ and $\text{Sh} = \text{CH}_2\text{OH}/\text{Lg} = \text{CH}_3$ show similar trends [2], but since the hydroxymethyl-terminated monolayers are wettable, the data are not as illustrative of disorder in the interface as $\text{Sh} = \text{CH}_3/\text{Lg} = \text{CH}_3$.

References

1. C.D. Bain, G.M. Whitesides *J. Am. Chem. Soc.* **110**, 3665 (1988); C.D. Bain, G.M. Whitesides *Science (Washington, D.C.)* **240**, 62 (1988); C.D. Bain, G.M. Whitesides *J. Am. Chem. Soc.* **111**, 7164 (1989).
2. J.P. Folkers, P.E. Laibinis, G.M. Whitesides *J. Am. Chem. Soc.* submitted for publication.
3. RCOOH on M_xO_y : W.C. Bigelow, D.L. Pickett, W.A. Zisman *J. Colloid Sci.* **1**, 513 (1946); Allara, D. L.; Nuzzo, R. G. *Langmuir* **1**, 45 (1985); Allara, D. L.; Nuzzo, R. G. *Langmuir* **1**, 52 (1985).
4. RNH_2 on M_xO_y : L.S. Bartell, R.J. Ruch *J. Phys. Chem.* **60**, 1231 (1956); Bartell, R.J. Ruch *J. Phys. Chem.* **63**, 1045 (1959); Bartell, J.F. Betts *J. Phys. Chem.* **64**, 1075 (1960).
5. $RSiCl_3$ on SiO_2 : J. Sagiv *J. Am. Chem. Soc.* **102**, 92 (1980); S.R. Wasserman, Y.-T. Tao, G.M. Whitesides *Langmuir* **5**, 1074 (1989).
6. RNC on Pt: J.J. Hickman, C. Zou, D. Ofer, P.D. Harvey, M.S. Wrighton, P.E. Laibinis, C.D. Bain, G.M. Whitesides *J. Am. Chem. Soc.* **111**, 7271 (1989).
7. RSSR on Au: R.G. Nuzzo, D.L. Allara *J. Am. Chem. Soc.* **105**, 4481 (1983); T.T.-T. Li, M.J. Weaver *J. Am. Chem. Soc.* **106**, 6107 (1984); R.G. Nuzzo, F.A. Fusco, D.L. Allara *J. Am. Chem. Soc.* **109**, 2358 (1987).
8. RSR on Au: E.B. Troughton, C.D. Bain, G.M. Whitesides, R.G. Nuzzo, D.L. Allara, M.D. Porter *Langmuir* **4**, 365 (1988).
9. RSH on Au: M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey *J. Am. Chem. Soc.* **109**, 3559 (1987).

10. RSH on Au: C.D. Bain, E.B. Troughton, Y.-T. Tao, J. Evall, G.M. Whitesides *J. Am. Chem. Soc.* **111**, 321 (1989).
11. RSH on Ag: M.M. Walczak, C. Chung, S.M. Stole, C.A. Widrig, M.D. Porter *J. Am. Chem. Soc.* **113**, 2370 (1991).
12. RSH on Au, Ag, Cu: P.E. Laibinis, G.M. Whitesides, D.L. Allara, Y.-T. Tao, A.N. Parikh, R.G. Nuzzo *J. Am. Chem. Soc.* **113**, 7152 (1991).
13. For general reviews on self-assembled monolayers and wetting, see: C.D. Bain, G.M. Whitesides *Angew. Chem., Int. Ed. Eng.* **28**, 506 (1989); G.M. Whitesides, P.E. Laibinis *Langmuir* **6**, 87 (1990).
14. For background information on SAMs, see: A. Ulman *An Introduction to Ultrathin Organic Films From Langmuir-Blodgett to Self-Assembly*. Academic Press, San Diego CA (1991).
15. R.G. Nuzzo, L.H. Dubois, D.L. Allara *J. Am. Chem. Soc.* **112**, 558 (1990); C.E.D. Chidsey, D.N. Loiacono *Langmuir* **6**, 682 (1990).
16. C.D. Bain, G.M. Whitesides *J. Am. Chem. Soc.* **110**, 6560 (1988); C.D. Bain, J. Evall, G.M. Whitesides *J. Am. Chem. Soc.* **111**, 7155 (1989); P.E. Laibinis, G.M. Whitesides *J. Am. Chem. Soc.* **114**, 0000 (1992).
17. X = alkyl ether: C.D. Bain, G.M. Whitesides *J. Am. Chem. Soc.* **110**, 5897 (1988).
18. X = carboxylic acid: C.D. Bain, G.M. Whitesides *Langmuir* **5**, 1370 (1989).
19. X = electroactive group: C.E.D. Chidsey, C.R. Bertozzi, T.M. Putvinski, A.M. Muzsice *J. Am. Chem. Soc.* **112**, 4301 (1990); J.J. Hickman, D. Ofer, C. Zou, M.S. Wrighton, P.E. Laibinis, G.M. Whitesides *J. Am. Chem. Soc.* **113**, 1128 (1991); J.J. Hickman, D.

- Ofer, P.E. Laibinis, G.M. Whitesides, M.S. Wrighton *Science* (Washington D.C.) **252**, 688 (1991).
20. X = polyethylene glycol: C. Pale-Grosdemange, E.S. Simon, K.L. Prime, G.M. Whitesides *J. Am. Chem. Soc.* **113**, 12 (1991); K.L. Prime, G.M. Whitesides *Science* (Washington D.C.) **252**, 1164 (1991).
21. X = group with large dipole: S.D. Evans, E. Urankar, A. Ulman, N. Ferris *J. Am. Chem. Soc.* **113**, 4121 (1991); S.D. Evans, K.E. Goppert-Berarducci, E. Urankar, L.J. Gerenser, A. Ulman, R.G. Snyder *Langmuir* **7**, 2700 (1991).
22. R.G. Nuzzo, E.M. Korenic, L.H. Dubois *J. Chem. Phys.* **93**, 767 (1990).
23. L. Strong, G.M. Whitesides *Langmuir* **4**, 546 (1988).
24. C.E.D. Chidsey, G.-Y. Liu, P. Rowntree, G. Scoles *J. Chem. Phys.* **91** 4421 (1989).
25. P. Fenter, P. Eisenberger, J. Li, N. Camillone III, S. Bernasek, G. Scoles, T.A. Ramanarayanan, K.S. Liang *Langmuir* **7**, 2013 (1991).
26. M.G. Samant, C.A. Brown, J.G. Gordon II *Langmuir* **7**, 437 (1991).
27. C.A. Widrig, C.A. Alves, M.D. Porter *J. Am. Chem. Soc.* **113**, 2805 (1991).
28. RSH on Au: M.A. Bryant, J.E. Pemberton *J. Am. Chem. Soc.* **113**, 8284 (1991); RSH on Ag: M.A. Bryant, J.E. Pemberton *J. Am. Chem. Soc.* **113**, 3629 (1991).
29. J. Hautman; M.L. Klein *J. Chem. Phys.* **91**, 4994 (1989); A. Ulman, J.E. Eilers, N. Tillman *Langmuir* **5**, 1147 (1989); J.

- Hautman, J.P. Bareman, W. Mar, M.L. Klein *J. Chem. Soc. Faraday Trans.* **87**, 2031 (1991).
30. C. Miller, P. Cuendet, M. Grätzel *J. Phys. Chem.* **95**, 877 (1991); C.E.D. Chidsey *Science (Washington, D.C.)* **251**, 919 (1991); C. Miller, M. Grätzel *J. Phys. Chem.* **95**, 5225 (1991).
31. C.D. Bain Ph.D. Thesis, Harvard University, (1988); P.E. Laibinis, R.L. Graham, H.A. Biebuyck, G.M. Whitesides *Science (Washington D.C.)* **254**, 981 (1991).
32. L.H. Dubois, B.R. Zegarski, R.G. Nuzzo *J. Am. Chem. Soc.* **112**, 570 (1990).
33. A. Ulman, S.D. Evans, Y. Schnidman, R. Sharma, J.E. Eilers, J.C. Chang *J. Am. Chem. Soc.* **113**, 1499 (1991).
34. G.M. Whitesides, H.A. Biebuyck, J.P. Folkers, K.L. Prime *J. Adhesion Sci. Technol.* **5**, 57 (1991).
35. J. Hautman, M.L. Klein *Phys. Rev. Lett.* **67**, 1763 (1991).
36. P.E. Laibinis, R.G. Nuzzo, G.M. Whitesides unpublished results.
37. C.D. Bain, G.M. Whitesides *J. Phys. Chem.* **93**, 1670 (1989); P.E. Laibinis, M.A. Fox, J.P. Folkers, G.M. Whitesides *Langmuir* **7**, 3167 (1991).
38. J.P. Folkers, P.E. Laibinis, G.M. Whitesides unpublished results.
39. For studies dealing with the kinetics of exchange, see D.M. Collard, M.A. Fox *Langmuir* **7**, 1192 (1991) and references therein.
40. V.M. Hallmark, S. Chiang, J.F. Rabolt, J.D. Swalen, R.J. Wilson *Phys. Rev. Lett.* **59**, 2879 (1987); C.E.D. Chidsey, N. Loiacono, T. Sleator, S. Nakahara *Surf. Sci.* **200**, 45 (1988); S.

- Buchholz, H. Fuchs, J.P. Rabe *J. Vac. Sci. Technol. B* **9**, 857 (1991).
41. J.J. Jasper *J. Phys. Chem. Ref. Data* **1**, 841 (1972).
42. J. Cognard *J. Chimie. Phys.* **84**, 357 (1987) and references therein.
43. For a general reference on wetting, see: P.G. de Gennes *Rev. Mod. Phys.* **57**, 827 (1985).
44. For examples of theoretical and experimental studies on hysteresis, see: R.N. Wenzel *Ind. Eng. Chem.* **28**, 988 (1936); R.J. Good *J. Am. Chem. Soc.* **74**, 5041 (1952); R.E. Johnson Jr., R.H. Dettre *Advances in Chemistry Series*, No. 43, American Chemical Society, Washington, D.C., 112 (1964); R.H. Dettre, R.E. Johnson Jr. *Advances in Chemistry Series*, No. 43, American Chemical Society, Washington, D.C., 136 (1964); J.F. Joanny, P.G. de Gennes *J. Chem. Phys.* **81**, 552 (1984); L.W. Schwartz, S. Garoff *Langmuir* **1**, 219 (1985).
45. T. Young *Philos. Trans. R. Soc. London* **95**, 65 (1805).
46. S.D. Evans, R. Sharma, A. Ulman *Langmuir* **7**, 156 (1991).
47. W.A. Zisman *Advances in Chemistry Series*, No. 43, American Chemical Society, Washington, D.C., 1 (1964) and references therein.
48. F.M. Fowkes *J. Phys. Chem.* **66**, 382 (1962); F.M. Fowkes *Advances in Chemistry Series*, No. 43, American Chemical Society, Washington, D.C., 99 (1964).

ABSTRACT DISTRIBUTION LIST

Prof. Robert W. Armstrong
Department of Chemistry
University of California
405 Hilgard Avenue
Los Angeles CA 90024

Dr. Joseph Boyer
Department of Chemistry
University of New Orleans
New Orleans LA 70148

Professor Jerald S. Bradshaw
Department of Chemistry
Brigham Young University
Provo UT 84602

Prof. Ronald Breslow
Department of Chemistry
Columbia University
New York NY 10027

Dr. Duncan W. Brown
Advanced Technology Materials
520-B Danbury Road
New Milford CT 06776

Prof. Cynthia J. Burrows
Department of Chemistry
State University of New York
Stony Brook NY 11794-3400

Professor Peter Chen
Department of Chemistry
Harvard University
Cambridge MA 02138

Prof. Anthony W. Czarnik
Department of Chemistry
Ohio State University
120 West 18th Avenue
Columbus OH 43210-1173

Prof. Peter Dervan
Department of Chemistry
Calif Institute of Technology
Pasadena CA 91125

Prof. Francois N. Diederich
Department of Chemistry
University of California
405 Hilgard Avenue
Los Angeles CA 90024

Prof. Dennis A. Dougherty
Department of Chemistry
Calif Institute of Technology
Pasadena CA 91125

Prof. Kenneth M. Doxsee
Department of Chemistry
University of Oregon
Eugene OR 97403

Prof. Margaret C. Etter
Department of Chemistry
University of Minnesota
207 Pleasant Street SE
Minneapolis MN 55455

Prof. Wilmer K. Fife
Department of Chemistry
Indiana Univ/Purdue Univ
1125 East 38th Street
Indianapolis IN 46223

Prof. Samuel H. Gellman
Department of Chemistry
University of Wisconsin
Madison WI 53706

Prof. Thomas J. McCarthy
Department of Polymer Science
University of Massachusetts
701 Graduate Research Center
Amherst MA 01003

Prof. Arthur E. Martell
Department of Chemistry
Texas A&M University
College Station TX 77843-3255

Prof. William L. Mock
Department of Chemistry
University of Illinois at Chicago
Chicago IL 60680

Prof. Martin E. Newcomb
Department of Chemistry
Texas A&M University
Box 3578
College Station TX 77843-3255

Prof. Peter Schultz
Department of Chemistry
University of California
Berkeley CA 94720

Prof. Carol Venanzi
Department of Chemistry
New Jersey Inst of Technology
323 King Blvd.
Newark NJ 07102

Prof. Howard W. Whitlock
Department of Chemistry
University of Wisconsin
Madison WI 53706

Prof. Jeffrey D. Winkler
Department of Chemistry
The University of Chicago
5735 S. Ellis Avenue
Chicago IL 60637

TECHNICAL REPORT DISTRIBUTION LIST

Office of Naval Research
Chemistry Division, Code 1113
800 North Quincy Street
Arlington VA 22217-5000

Defense Technical Information
Center
Building 5, Cameron Station
Alexandria VA 22314

Dr. James S. Murday
Chemistry Division, Code 6100
Naval Research Laboratory
Washington DC 20375-5000

Dr. Robert Green, Director
Chemistry Division, Code 385
Naval Weapons Center
China Lake CA 93555-6001

Dr. Eugene C. Fischer
Code 2840
David Taylor Research Center
Annapolis MD 21402-5067

Dr. Elek Lindner
Naval Ocean Systems Center
Code 52
San Diego CA 92152-5000

Commanding Officer
Naval Weapons Support Center
Attn: Dr. Bernard E. Douda
Crane IN 47522-5050

Dr. Richard W. Drisko
Naval Civil Engineering
Laboratory
Code L52
Fort Hueneme CA 93043

Dr. Harold H. Singerman
David Taylor Research Center
Annapolis MD 21402-5067
ATTN: Code 283

Chief of Naval Research
Special Assistant for Marine
Corps Matters, Code 00MC
800 North Quincy Street
Arlington VA 22217-5000