Self-assembled monolayers of alkanethiols on gold: the adsorption and wetting properties of monolayers derived from two components with alkane chains of different lengths

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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 $(HS(CH_2)_{10}Sh)$ 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_2OH were investigated: $Sh = CH_3/Lg = CH_2OH$, $Sh = CH_2OH/Lg = CH_3$, $Sh = CH_2OH/Lg = CH_2OH$, and $Sh = CH_3/Lg = CH_3$. The compositions of these SAMs are not the same as the compositions of the solutions from which they were formed. Although the relationship between the composition of the SAM and the composition of the solution suggests that some phase separation may be occurring within the SAM, contact angles with water and hexadecane show that significant disorder still remains in the interfacial region.

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—$HS(CH_2)_{sh}Sh$ and $HS(CH_2)_{lg}Lg$, where $sh = 10$ and $lg = 21$, 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 $(Sh = CH_3/Lg = CH_3$, $Sh = CH_3/Lg = CH_2OH$, $Sh = CH_2OH/Lg = CH_3$, and $Sh = CH_2OH/Lg = CH_2OH)$. 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 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 (general

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formula HS(CH$_2$)$_n$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 mono-layers [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 and atomic force microscopies [27], and surface Raman spectroscopy [28] (Fig. 1); molecular dynamics calculations yield a general structure in agreement with these techniques [29]. The experimentally determined 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 on 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 or 'mixed' SAMs [1, 2, 13, 16, 18, 20]. The latter method provides a greater degree of control over the properties of the interface, because the relative concentrations of the two components in the SAM can be adjusted.

When two-component SAMs are used to form surfaces of specific wettabilities, two relationships determine the wettability: the relationship between the wettability of the surface and the composition of the SAM, and the relationship
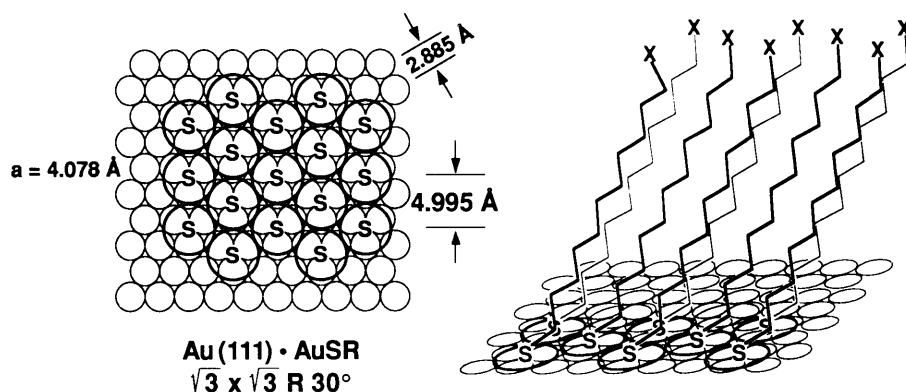

Figure 1. The structure of alkanethiolates adsorbed on gold (111). Thiolates are adsorbed at three-fold hollows on the surface forming a commensurate $\sqrt{3} \times \sqrt{3}$ R30° structure [23–26]. The alkyl chains are in a *trans* zig-zag array (the small concentration of *gauche* conformers is localized near the ends of the chains [12, 24, 29]) and are oriented about 30° from the surface normal [9, 12, 15, 22]. Because of this highly ordered structure, the tail groups (X) are localized at the monolayer–air interface.

between the composition of the SAM and the composition of the solution. In this paper we discuss both of these relationships by presenting data for SAMs derived from two alkanethiols with alkyl chains of different lengths. We also discuss the wetting results in terms of the effect of disorder in the interfacial region on the wettability of these two-component SAMs [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 Fig. 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 information pertaining to elemental composition and oxidation states in addition to the relative concentrations of the two components in a SAM. In this paper, we
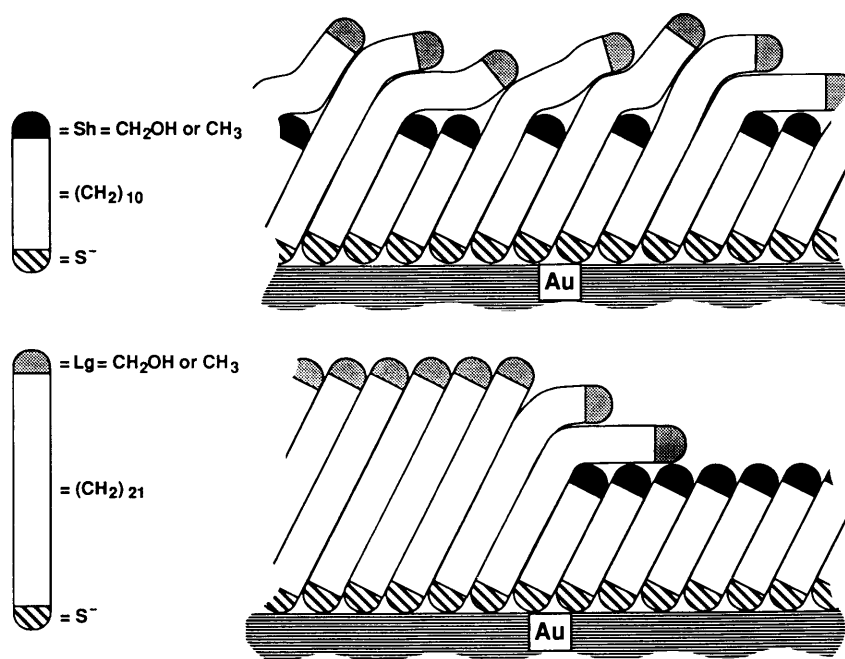
Figure 2. Schematic representation of a mixed SAM with equal concentrations of a long-chain (Lg) and a short-chain (Sh) thiolate (ratio of the two components in the SAM $= R_{s,xM} = [Lg]/[Sh] = 1$; mole fraction of the longer component in the SAM $= \chi_{1g, s,xM} = [Lg]/([Lg] + [Sh]) = 0.5$). The 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.

have used the natural logarithm of the ratio of the carbon 1s intensity to the gold 4f intensity (denoted as $\ln[C(1s)/Au(4f)]$ in this paper) 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 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, 16]. 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†

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; 1 day; room temperature), the ratio of the concentrations of the two thiolates in the SAM ($R_{SAM} = [Au(I)^-S(CH_2)_{lg}Lg]/[Au(I)^-S(CH_2)_{sh}Sh]$) and the ratio of the concentrations of the respective thiols in solution ($R_{soln} = [HS(CH_2)_{lg}Lg]/[HS(CH_2)_{sh}Sh]$) are not the same (Fig. 3). In Fig. 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 $\chi_{Lg,SAM} + \chi_{Sh,SAM} = 1$) against R_{SAM} [1, 2]. The deviation of this curve from ideality ($R_{SAM} = R_{soln}$; dashed line in Fig. 3) indicates a preference of the longer component for the surface; the sharpness of the transition region suggests that mixing of the two components is not enthalpically favored within the SAM, possibly leading to phase separation in the SAMs.‡ From the relationship between the composition of the SAM and the composition of the solution, we infer the following qualitative energy ranking for interactions within the SAM: $Lg \cdot Lg > Sh \cdot Sh > Lg \cdot Sh$. 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

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*For details concerning the experimental procedures, see ref. 2.

†In this section, we have used the system $Sh = CH_3/Lg = CH_2OH$ to illustrate the relationship between the composition of the SAMs and the composition of the solutions; the general trends are the same for the other systems that we have studied [2, 38].

‡At present, we do not have experimental results that explicitly determine the origin of the inferred phase separation in these SAMs. In a separate paper, we will present a thorough analysis of the experimentally observed relationship between the composition of the SAM and the composition of the solution in comparison to a theoretical model of the formation of mixed SAMs [38].
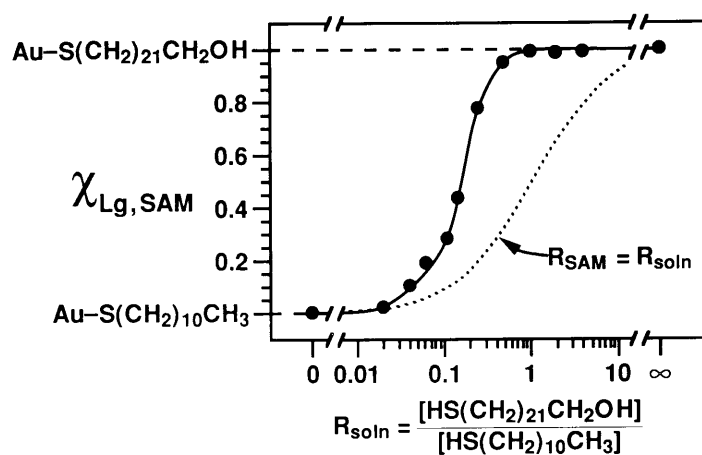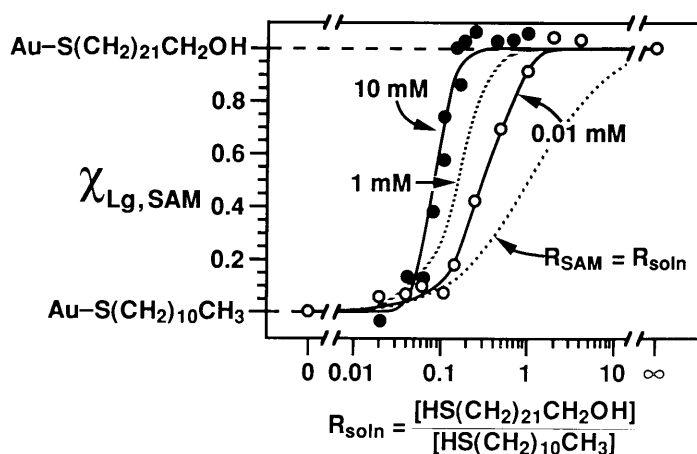
Figure 3. Comparison of the compositions of SAMs and of the solutions from which they were formed: mixed SAMS formed from the competitive adsorption of $HS(CH_2)_{21}CH_2OH$ and $HS(CH_2)_{10}CH_3$ (experimental conditions: ethanolic solutions with a total concentration of thiol of 1 mM; room temperature; 1 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 ($\chi_{Lg,SAM}$, where $\chi_{Lg,SAM} + \chi_{Sh,SAM} = 1$), determined from the logarithm of the ratio of the intensity of the carbon (1s) peak in XPS to that of the gold (4f) peak [37]. Some data points may have $\chi_{Lg,SAM} < 0$ or $\chi_{Lg,SAM} > 1$ because of errors in the measurements. If the intensities of both the carbon (1s) signal and the gold (4f) signal vary by about ±5%, then the values of ln(C/Au) vary by ±7%, resulting in a minimum error of ±7% in the values of $\chi_{Lg,SAM}$. We have left these data points outside $\chi_{Lg,SAM} = 0$ and $\chi_{Lg,SAM} = 1$ (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 $R_{SAM} = R_{soln}$.

increase in the preference for the longer component in the SAM, and also an increase in the sharpness of the transition region (Fig. 4). When the total concentration of thiol was decreased, the preference for the longer component and the sharpness of the transition region decreased (Fig. 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 $Sh = CH_2OH/Lg = CH_3$, 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,* 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

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*We have not systematically addressed the influence of the 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].

$$R_{soln} = \frac{[HS(CH_2)_{21}CH_2OH]}{[HS(CH_2)_{10}CH_3]}$$

Figure 4. Comparison of the 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 $HS(CH_2)_{21}CH_2OH$ and $HS(CH_2)_{10}CH_3$ from ethanolic solutions with total concentrations of thiol of 10 mM at room temperature for 1 day. Open circles: Mixed SAMs formed from the competitive adsorption of $HS(CH_2)_{21}CH_2OH$ and $HS(CH_2)_{10}CH_3$ from ethanolic solutions with total concentrations of thiol of 0.01 mM at room temperature for 1 day. Axis labels are described in the caption to Fig. 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 Fig. 3; the dashed curve on the right represents $R_{SAM} = R_{soln}$.

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 ($\gamma_{LV}^{H_2O} \approx 73$ mJ/m^2; $\gamma_{LV}^{HD} \approx 28$ mJ m^{-2} 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 that 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 in contact angles 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 his section were taken on SAMs formed under normal adsorption conditions. Up to now, 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).

4.1. 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 (Fig. 5, bottom). In this system ($Sh = CH_3/Lg = CH_2OH$), both the advancing and the receding contact angles are, however, linearly related to the
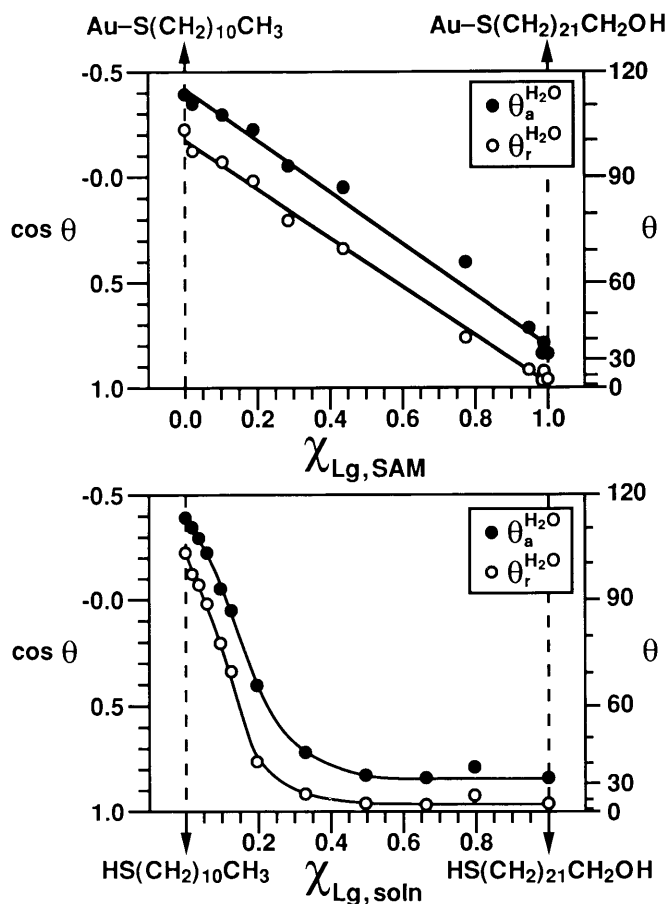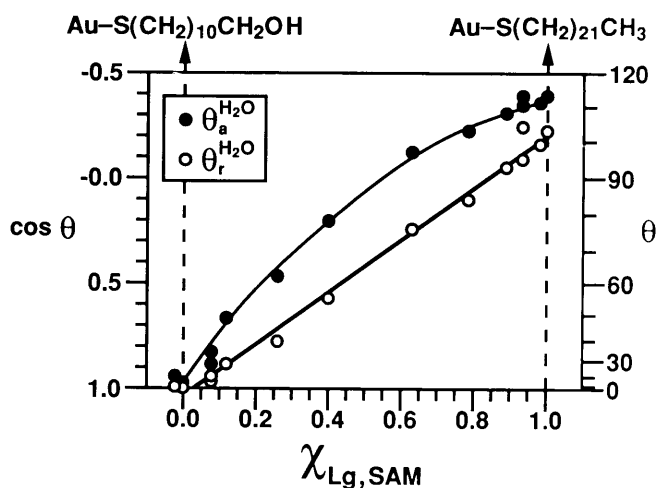

Figure 5. Advancing (filled circles) and receding (open circles) contact angles of water on mixed SAMs obtained by the competitive adsorption of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{21}CH_2OH$ onto gold as a function of the mole fraction of the longer component in the SAM, $\chi_{Lg,SAM}$ (top), and as a function of the mole fraction of the longer component in solution, $\chi_{Lg,soln}$ (bottom). Values of $\chi_{Lg,SAM}$ were determined as described in the caption to Fig. 3; $\chi_{Lg,soln} = R_{soln}/(1 + R_{soln})$. 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.

composition of the SAM (i.e. $\chi_{Lg,SAM}$; Fig. 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 (Fig. 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 the advancing angles to 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 receding, the SAM could reorganize to uncover the hydroxymethyl groups.

When both tail groups are hydroxymethyl (i.e. $Sh = CH_2OH/Lg = CH_2OH$), the mixed SAMs are considerably more hydrophobic than the single-component SAMs (Fig. 7). The advancing contact angle increases from about $20°$ for the pure SAMs to $54°$ for the SAM with $\chi_{Lg,SAM} \approx 0.5$. This change corresponds to a decrease in the interfacial free energy of the system $(\gamma_{sv} - \gamma_{sl})$ of $\sim 25 \, mJ/m^2$ (or $\sim 0.8 \, kcal/mol$ of surface groups, assuming a constant concentration of surface groups of $8 \times 10^{-10} \, mol/cm^2$ [23, 24, 27]). We observed previously that the advancing contact angle of water on mixed SAMs derived from $HS(CH_2)_{10}CH_2OH$ and $HS(CH_2)_{18}CH_2OH$ increased to $41°$ from $\sim 10°$ on the

Figure 6. Advancing (filled circles) and receding (open circles) contact angles of water on mixed SAMs obtained by the adsorption of $HS(CH_2)_{10}CH_2OH$ and $HS(CH_2)_{21}CH_3$ 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 Fig. 3. The straight line through the receding angles was determined by a least-squares fit. The curve through the data of the advancing contact angles is only a guide to the eye.
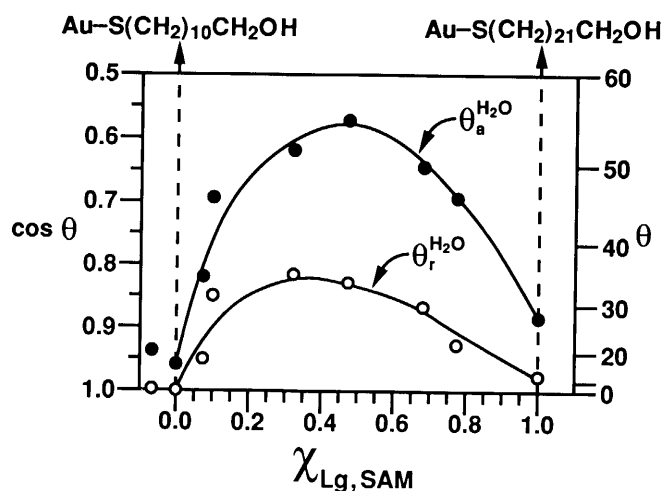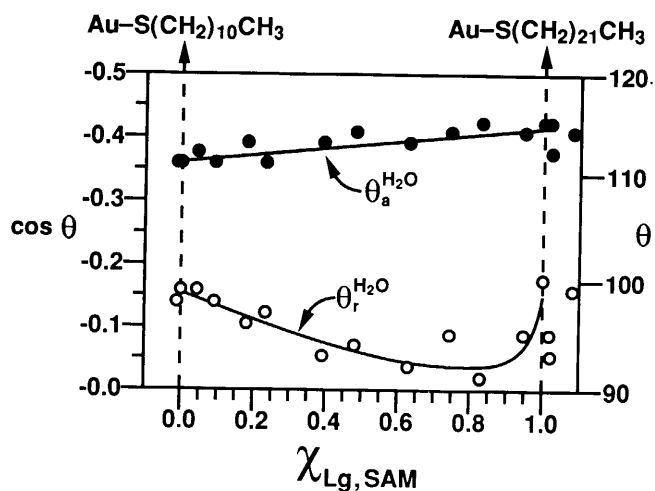
Figure 7. Advancing (filled circles) and receding (open circles) contact angles of water on mixed SAMs obtained by the adsorption of $HS(CH_2)_{10}CH_2OH$ and $HS(CH_2)_{21}CH_2OH$ onto gold as a function of the mole fraction of the longer component in the SAM. The mole fractions were determined as described in the caption to Fig. 3. The curves through the data are only guides to the eye.

single component SAMs ($\gamma_{SV} - \gamma_{SL}$ decreases by 17 mJ/m² or 0.5 kcal/mol) [1].* 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. These results 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 mixing of the components because we do not know the extent to which these components may be forming islands on the surface.

Mixed phases of $Sh = CH_3/Lg = CH_3$ are as hydrophobic (as determined by the advancing contact angle of water) as the highly ordered, single-component SAMs (Fig. 8). While the contact angles of hexadecane clearly show that the interface is disordered (see Fig. 9), the advancing contact angle of water is unaffected by the presence of methylene groups at the interface. Generally, a surface composed of methyl groups has a γ_{SV} of about 20 mJ/m², and one of methylene groups, $\gamma_{SV} \approx 30$ mJ m² (e.g. polyethylene) [47]; this difference should lead to a decrease in the equilibrium contact angle of water by ~8° using Fowkes's equation for non-polar surfaces [48]: $\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\sqrt{\gamma_{SV}\gamma_{LV}^d}$, where the superscript d refers to the dispersive component of the surface tension of the liquid ($\gamma_{LV}^d \approx 22$ mJ/m² for water at room temperature [42]). 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

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*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 the adsorption of airborne contaminants to this high-energy surface, and not to reconstruction of the monolayer–air interface of the single-component SAMs [46].
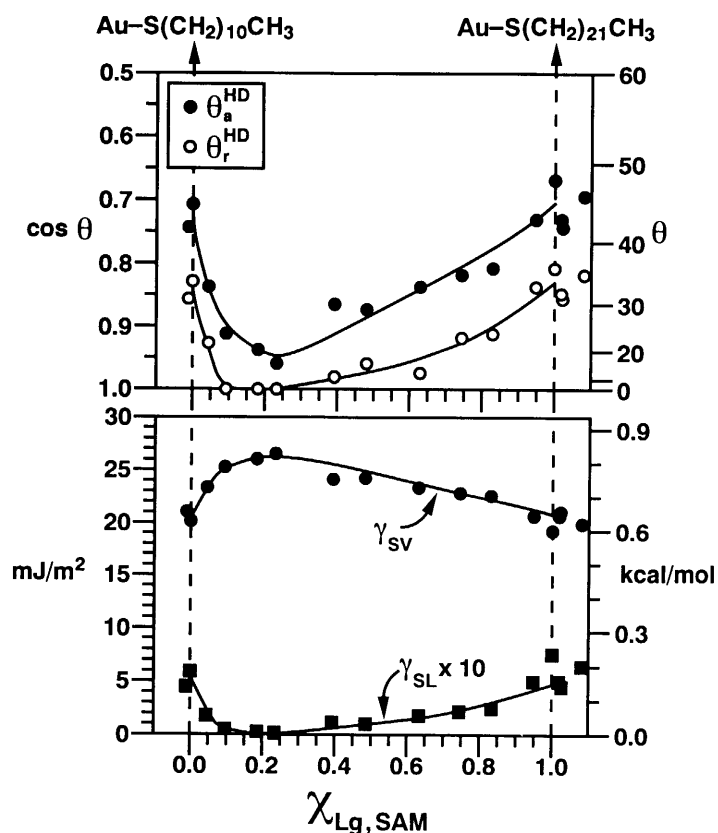
Figure 8. Advancing (filled circles) and receding (open circles) contact angles of water on mixed SAMs obtained by the adsorption of HS(CH₂)₁₀CH₃ and HS(CH₂)₂₁CH₃ onto gold as a function of the mole fraction of the longer component in the SAM. The mole fractions were determined as described in the caption to Fig. 3. The curves through the data are only guides to the eye.

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.

4.2. 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 ~45° on the single-component SAMs to 16° (Fig. 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's equation [48] to determine the solid–vapor and solid–liquid interfacial tensions of these SAMs (Fig. 9, bottom). The maximum decrease in the advancing contact angle of hexadecane from the values on the single-component SAMs corresponds to an increase in γ_{SV} by about 6.5 mJ/m² (0.20 kcal/mol of surface groups) and a decrease in γ_{SL} by about 0.6 mJ/m² (0.02 kcal/mol of surface groups).* 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.

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*The advancing contact angles of hexadecane on $Sh = CH_3/Lg = CH_2OH$ and $Sh = CH_2OH/Lg = CH_3$ show similar trends [2], but since the hydroxymethyl-terminated monolayers are wettable, the data are not as illustrative of disorder in the interface as they are for $Sh = CH_3/Lg = CH_3$.

Figure 9. Top: Advancing (filled circles) and receding (open circles) contact angles of hexadecane on mixed SAMs obtained by the adsorption of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{21}CH_3$ 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's equation [48]. Values of γ_{SL} have been multiplied by 10 to bring them on scale. The mole fractions were determined as described in the caption to Fig. 3. The curves through the data are only guides to the eye.

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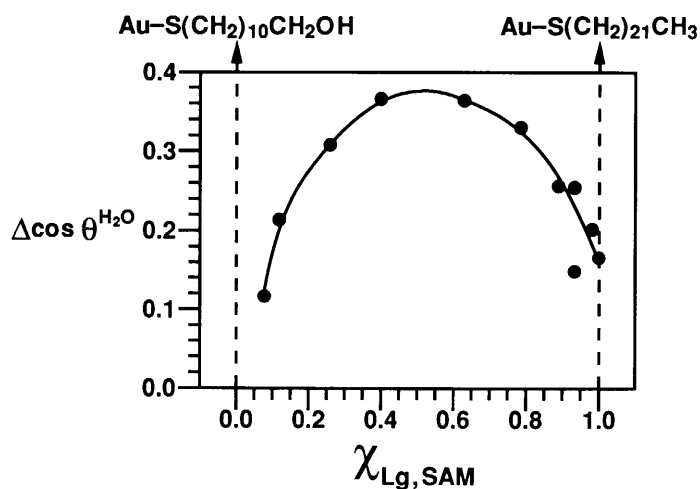
Figure 10. Hysteresis in the contact angle of water on mixed SAMs obtained by the adsorption of HS(CH$_2$)$_{10}$CH$_2$OH and HS(CH$_2$)$_{21}$CH$_3$ onto gold as a function of the mole fraction of the longer component on the surface. Values of hysteresis cannot be determined when the receding angle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

5. CONCLUSIONS

The data summarized in this paper illustrate that formation of two-component self-assembled monolayers of alkanethiolates on gold is an excellent method for forming surfaces with controlled wettabilities. When using SAMs to form such surfaces, the composition of the SAM may not equal the composition of the solution, and the relationship between these two may be dependent on the conditions used to form the monolayers. Factors such as the total concentration of thiol in the solution, the length of time that the samples were left in solution, the temperature of the solution, and the solvent used are extremely important in determining the composition of the SAM [1, 16, 38].

The data also illustrate that two-component SAMs 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 Sh = CH$_2$OH/Lg = CH$_2$OH, but is only slightly sensitive to the increase in the concentration of methylene groups in the interfacial regions of mixed SAMs of Sh = CH$_3$/Lg = 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 Sh = CH$_3$/Lg = CH$_3$. Hysteresis in 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 con-

ditions for adsorption (see last footnote on p. 1401). 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 within SAMs, and then relating the wetting properties (especially hysteresis) to the heterogeneity of the interfaces.

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