make six key observations regarding mixed monolayers:

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

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

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

(4) The two components of the monolayer do not act independently in determining the wettability of the surface. Polar groups are more hydrophilic when they are in the nonpolar environment provided by methyl groups than when the surface of the monolayer is composed largely of other polar groups.

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

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

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

Registry No. Au, 7440-57-5; $CH_3(CH_2)_{14}CH_3$, 544-76-3; $HS(CH_2)_{10}CH_2OH$, 73768-94-2; $[S(CH_2)_{10}CH_2OH]_2$, 119438-02-7; $[S(CH_2)_{10}CH_3]_2$, 79458-27-8; $HS(CH_2)_{10}CO_2H$, 71310-21-9; $HS(CH_2)_{10}CH_2Br$, 116129-34-1; $HS(CH_2)_8CN$, 117559-63-4; $HS(CH_2)_8CH_3$, 1455-21-6; $HS(CH_2)_{10}CH_3$, 5332-52-5; $HS(CH_2)_{11}CH_3$, 112-55-0; $HS(CH_2)_{15}CH_3$, 2917-26-2; $HS(CH_2)_{18}CH_3$, 53193-23-0; $HS(CH_2)_{21}CH_3$, 7773-83-3; $HS(CH_2)_{18}CH_2OH$, 114896-31-0; $Br(CH_2)_{18}CH_2OH$, 121497-31-2; 1,8-dibromooctane, 4549-32-0; 11-undecenylmagnesium bromide, 88476-93-1; 19-bromo-1-nonadecene, 121497-30-1; disiamylborane, 1069-54-1.

Supplementary Material Available: Details of the synthesis of $HS(CH_2)_{19}OH$, the competitive adsorption of thiols with phosphines, isonitriles, and disulfides, and the measurement of surface compositions by XPS (7 pages). Ordering information is given on any current masthead page.

Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Length of the Alkyl Chain[1]

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Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received October 24, 1988*

Abstract: Mixtures of two long-chain alkanethiols, $HS(CH_2)_nX$ and $HS(CH_2)_mY$ (X, Y = CH_3, OH; $n > m$), in which the alkyl chains have different lengths, adsorb from solution onto gold and form monolayers comprising a densely packed inner region adjacent to the gold surface and a disordered outer region in contact with the solution. When X = Y = CH_3 ($n \neq m$), this disordered phase makes the "mixed monolayer" more oleophilic than the ordered, pure (i.e., single-component) monolayers. When X = Y = OH, the pure monolayers are wetted by water, but the mixed monolayers are less hydrophilic because nonpolar polymethylene chains are exposed at the surface. When X = CH_3, Y = OH (n = 21, m = 11), a very sharp transition occurs from a monolayer composed largely of the longer, methyl-terminated component to the shorter, hydroxyl-terminated component as the mole fraction of $HS(CH_2)_{11}OH$ in the adsorption solution is increased. From solutions containing two thiols, adsorption of the thiol with the longer chain is preferred. This preference is greater when the monolayers are adsorbed from ethanol than from isooctane. The mixed monolayers do not act as ideal two-dimensional solutions. The adsorption isotherms suggest a positive excess free energy of mixing of the two components in the monolayer. The compositions of the monolayers appear to be determined largely by thermodynamics, although in some cases there is also a kinetic contribution. The two components in the mixed monolayers do not phase-segregate into macroscopic islands (greater than a few tens of angstroms across) but are probably not randomly dispersed within the monolayer. The wettability of mixed, methyl-terminated monolayers can be partially rationalized by the geometric mean approximation, but a full description probably requires inclusion of the entropy of mixing at the monolayer–liquid interface. The hysteresis in the contact angle on these monolayers cannot be explained by theories of wetting based on macroscopic heterogeneity. Contact angles are more sensitive than optical ellipsometry or X-ray photoelectron spectroscopy to certain types of changes in the composition and structure of these monolayers.

Long-chain alkanethiols, $HS(CH_2)_nX$, adsorb from solution onto gold and form densely packed monolayer films.[3-5] This paper is the second of two that present studies of the "mixed monolayers" formed by the coadsorption of two thiols. In the preceding paper

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in this issue,[6] we discussed the influence of the tail group, X, and the nature of the solvent on the formation of monolayer films on gold and on the properties of the resulting surfaces. In this paper, we turn our attention to monolayers formed by coadsorption of two thiols, $HS(CH_2)_nX$ and $HS(CH_2)_mY$ ($n > m$), that differ in the length of the polymethylene chain.

We present data here for mixed monolayers in three general classes: (a) both thiols terminated by methyl groups ($X = Y = CH_3$, $n \neq m$); (b) both thiols terminated by hydroxyl groups ($X = Y = OH$);[7] (c) a long-chain thiol terminated by a methyl group and a short-chain thiol terminated by a hydroxyl group ($X = CH_3$, $Y = OH$).[8] We define a parameter, R, to be the ratio *in solution* of the concentration of the species with the shorter chain to the species with the longer chain: $R = [HS(CH_2)_mY]_{sol}/[HS(CH_2)_nX]_{sol}$ ($n > m$). We have previously published preliminary results from the latter two systems as communications.[7,8]

The strategy, as in the previous paper, was to adsorb monolayers onto gold from dilute solutions containing a mixture of two thiols at varying mole fractions but fixed total thiol concentration. The resulting monolayers were then characterized by ellipsometry, X-ray photoelectron spectroscopy (XPS), and measurement of contact angles.

The contact angles of mixed monolayers provide a sensitive probe of their structure. Long-chain thiols form well-packed, pseudocrystalline, oriented monolayers on gold in which the hydrocarbon chains are all-trans and canted ~30° from the normal to the surface (Figure 1A,C).[4,9] Methyl-terminated thiols generate surfaces that are composed of a densely packed array of methyl groups and are both hydrophobic ($\theta_a(H_2O) = 112°$) and oleophobic ($\theta_a(HD) = 47°$; HD = hexadecane).[3] Hydroxyl-terminated thiols form monolayers that are wetted by both hexadecane and water ($\theta_a(H_2O) = \theta_a(HD) \sim 0°$).[7] If two thiols with the same tail group but different chain lengths were to separate into discrete macroscopic islands, then the wettability of the mixed monolayers would be the same as that of the pure monolayers (Figure 1D). A more interesting situation would arise if the two components were dispersed on a molecular scale. The inner part of the monolayer, adjacent to the gold surface, would still be well-packed.[10] The free volume introduced into the outer part of the monolayer by the presence of the shorter chains would result in gauche bonds and a loss of lateral and orientational order: the outer part of the monolayer would be disordered and liquidlike (Figure 1B). The presence of this disordered phase would be evident as a large deviation in the contact angles from the values observed on the pure monolayers. If both thiols were terminated by hydroxyl groups, the nonpolar methylene groups exposed in the mixed monolayers would raise the contact angle of water relative to the pure monolayers. If both thiols were terminated by methyl groups, the surface of the mixed monolayers would resemble a liquid hydrocarbon. Since any liquid spreads on a surface composed of the same liquid, we would expect hexadecane to exhibit a much lower contact angle on the mixed monolayers than on the pure monolayers. Our experiments support disorder in the outer phase.

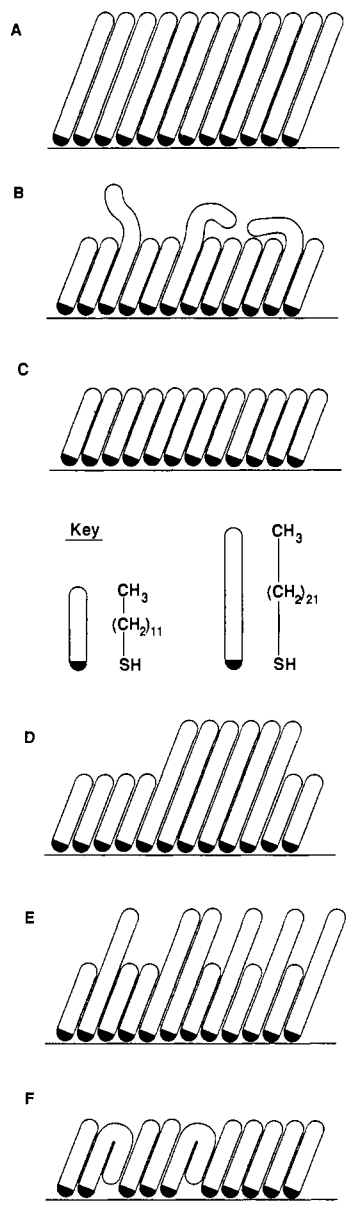

Figure 1. Schematic illustration of monolayers of thiols on gold. (A) Pure monolayer of docosanethiol. (B) Mixed monolayer of docosanethiol and dodecanethiol near the composition that yielded the lowest contact angles with hexadecane. (C) Pure monolayer of dodecanethiol. (D–F) Structures that we believe do not occur in the monolayers studied here. (D) Mixtures of docosanethiol and dodecanethiol phase-separated into islands that have the properties of the pure monolayers are not consistent with the observed contact angles. (E) An oriented monolayer with the two components dispersed on a molecular scale is unstable relative to (B). (F) Hairpin loops in the thiol with the longer chain are energetically unstable with respect to incorporation of additional molecules of a thiol into the monolayer.

By using monolayers containing chains of different length, we can control the degree of disorder at interfaces and vary the structure perpendicular to the surface. There are many reasons for interest in such systems. By relating the contact angle and the hysteresis in the contact angle to the structure of a surface, we can test theories of wetting.[11-14] Current theories of wetting

(1) Supported in part by the ONR and by DARPA. The XPS was provided by DARPA through the University Research Initiative and is housed in the Harvard University Materials Research Laboratory (an NSF-supported laboratory).

(2) IBM Pre-Doctoral Fellow in Physical Chemistry, 1985–1986.

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

(4) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559–3568.

(5) Bain, C. D. Ph.D. Thesis, Harvard, Cambridge, MA, 1988.

(6) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, preceding paper in this issue.

(7) Bain, C. D.; Whitesides, G. M. *Science (Washington, D.C.)* **1988**, *240*, 62–63.

(8) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3665–3666.

(9) Nuzzo, R. G., private communication.

(10) Experiments are in progress to determine whether there is any disorder in the inner part of the monolayer adjacent to the gold surface. In Langmuir–Blodgett monolayers of alcohols with different chain lengths, the area per molecule was found to be slightly greater than that expected on the basis of the areas per molecule in monolayers of the two pure alcohols. This discrepancy was interpreted as arising from disorder extending partially into the inner phase (Shah, D. O.; Shiao, S. Y. In *Monolayers*; Goddard, E. D., Ed.; Advances in Chemistry Series 144; American Chemical Society: Washington, DC, 1975; pp 153–164).

(11) Johnson, R. E.; Dettre, R. H. *J. Phys. Chem.* **1964**, *68*, 1744–1750. Schwartz, L. W.; Garoff, S. *Langmuir* **1985**, *1*, 219–230. Schwartz, L. W.; Garoff, S. *J. Colloid Interface Sci.* **1985**, *106*, 422–437. Pomeau, Y.; Vannimenus, J. *J. Colloid Interface Sci.* **1985**, *104*, 477–488.

are based on the consideration of the enthalpy of intermolecular interactions and do not specifically include the interfacial entropy except insofar as it scales with the enthalpy. Specifically, current theories do not incorporate entropy of mixing at the solid-liquid interface. Since the variation in the degree of order at a solid-liquid interface changes the interfacial entropy, any model that seeks to provide a full description of wetting in these systems will have to address the role of entropy. We have also attempted to reconcile the hysteresis observed in the contact angle with the predictions of theories based on macroscopic heterogeneity and conclude that hysteresis in these systems is determined by the microscopic structure of the surface.

Mixed monolayers containing components of different chain lengths could potentially be used to construct cavities of a controlled size containing specific functional groups.[15] Such systems would be useful for modeling enzyme activity, molecular recognition, heterogeneous catalysis, and electrode processes. Control over the tail groups exposed at the monolayer-liquid interface permits the study of the effect of the environment on acidity/basicity and chemical reactivity at interfaces. The mixed methyl-terminated chains provide a model system for synthetic membranes incorporating lipids of mixed chain lengths.[16] Direct applications also exist in the modification of wetting and adhesion, in chromatography,[17] and perhaps in electronic devices.[18]

Experimental Section

Details of the purification and synthesis of the materials used in these studies and a general description of procedures have been provided in the preceding paper.[6]

Both ellipsometric thicknesses and XPS intensities were used to calculate the composition of monolayers containing two components with different chain lengths. The ellipsometric readings were converted to compositions on the assumption that the ellipsometric thickness is a linear function of the composition. There is no a priori reason why this assumption should be valid, since the optical constants of the mixed monolayers might differ from those of the pure monolayers. Radiotracer measurements on partial monolayers of octadecylamine on chromium[19] supported a linear relationship, however, so our approximation is probably sound.

The compositions of monolayers comprising two methyl-terminated thiols were calculated from the ratio of the intensities of the C(1s) and Au($4f_{7/2}$) photoelectrons. If the monolayers are homogeneous (i.e., they do not comprise single-component domains), the C/Au ratio is given to a good approximation by[20]

$$\frac{C}{Au} = \frac{C_\infty(1 - e^{-d/\lambda_1 \sin\theta})}{Au_0 e^{-d/\lambda_2 \sin\theta}} \quad (1)$$

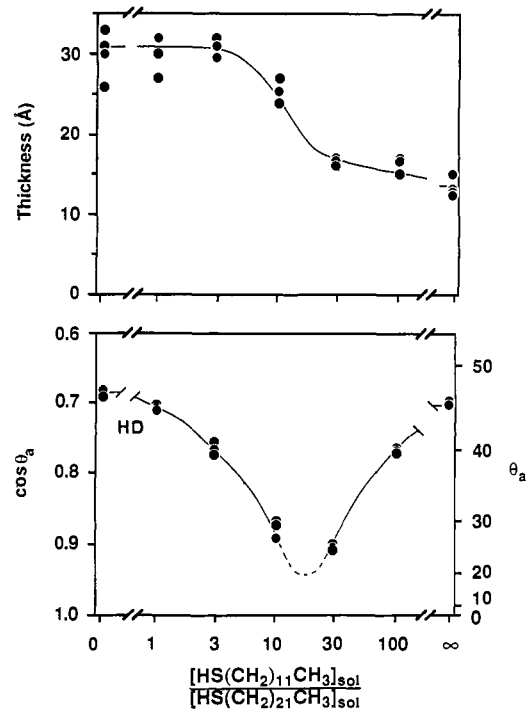

Figure 2. Monolayers adsorbed onto gold from ethanolic solutions containing mixtures of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$: ellipsometric thickness (upper figure) and advancing contact angle of hexadecane (lower figure) are plotted against the ratio of $HS(CH_2)_{11}CH_3$ to $HS(CH_2)_{21}CH_3$ in solution. The line in the lower figure has been added as an aid to the eye; we cannot determine from these data alone the minimum value of θ_a(HD) attainable.

where C_∞ is the C(1s) intensity from an infinitely thick monolayer of an alkanethiol on gold, Au_0 is the Au($4f_{7/2}$) intensity from a clean gold surface, θ is the angle between the axis of the analyzer and the surface horizontal (the take-off angle), λ_1 is the attenuation length of C(1s) photoelectrons in a hydrocarbon film (~36 Å), λ_2 is the attenuation length of Au($4f_{7/2}$) photoelectrons in a hydrocarbon film (~42 Å), and d is the thickness of the monolayer. We could use this formula directly to calculate the thickness and hence the composition of the monolayers. In practice, it is easier to calibrate the C/Au ratio against actual monolayers of pure alkanethiols with various chain lengths. The C/Au ratios from the mixed monolayers shown in Figure 3 were compared with the C/Au ratio obtained from pure monolayers of $HS(CH_2)_nCH_3$ adsorbed from ethanol.[20] Since the acquisition parameters were different in the two experiments, the ratios were normalized to the same value of C/Au for monolayers of $HS(CH_2)_{11}CH_3$. With this normalization, the C/Au ratio for the pure monolayer of $HS(CH_2)_{21}CH_3$ adsorbed from isooctane corresponded to a monolayer 21.5 carbons thick adsorbed from ethanol. For each mixed monolayer, we determined an *equivalent chain length* of a pure monolayer of an alkanethiol on gold. Finally, we calculated the composition of the monolayer on the assumption that the composition was a linear function of the equivalent chain length, i.e., that attenuation of the photoelectrons is determined only by the mass of the hydrocarbon film per unit surface area and not by the structure of the film.

Results

$HS(CH_2)_{21}CH_3$ + $HS(CH_2)_{11}CH_3$ Adsorbed from Ethanol. Preliminary experiments in which gold slides were immersed in solutions containing 1:1 mixtures of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_nCH_3$ (n = 6-18) in ethanol resulted in each case in a monolayer derived almost exclusively from docosanethiol. To form mixed monolayers of different chain lengths from ethanol, mass action must be used to drive the incorporation of the shorter chain into the monolayer. Figure 2 shows the ellipsometric thickness and the advancing contact angle of hexadecane (HD) on monolayers adsorbed from ethanolic solutions containing $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ in the ratio R = $[HS(CH_2)_{11}CH_3]_{sol}/[HS(CH_2)_{21}CH_3]_{sol}$ in the range 1-100, together with monolayers of the two pure thiols. Both pure monolayers

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(14) de Gennes, P.-G. *Rev. Mod. Phys.* **1985**, *57*, 827-863.
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(18) Recently there has been much interest in the measurement of intermolecular interactions with Tabor force balances (Tabor, D.; Winterton, R. H. S. *Proc. R. Soc. London, Ser. A* **1969**, *312*, 435. Israelachvili, J. N. *Acc. Chem. Res.* **1987**, *20*, 415-421. Israelachvili, J. N.; McGuiggan, P. M. *Science (Washington, D.C.)* **1988**, *241*, 795-800). Atomically smooth gold films can be formed on mica plates of the type normally used in force balance measurements (Hallmark, V. M.; Chiang, S.; Rabolt, J. F.; Swalen, J. D.; Wilson, R. J. *Phys. Rev. Lett.* **1987**, *59*, 2879-2882. Chidsey, C. E. D.; Loiacono, D. N.; Sleater, T.; Nakahara, S. *Surf. Sci.* **1988**, *200*, 45-66). Monolayers on gold are more densely packed than monolayers of ammonium salts on mica ($\theta_a(H_2O)$ = 95° for dihexadecyldimethylammonium acetate on mica (Pashley, R. M.; McGuiggan, P. M.; Ninham, B. W.; Evans, D. F. *Science (Washington, D.C.)* **1985**, *229*, 1088-1089. Christenson, H. K. *J. Phys. Chem.* **1986**, *90*, 4-6)) and, as we show in these papers, offer great flexibility over the structure at the monolayer-liquid interface. In addition, monolayers of thiols on gold should prevent the leaching of ions from the mica into solution, thus eliminating the effects of the electrostatic double layer. The problem of measuring the spacing between two opaque substrates can be avoided by using gold films sufficiently thin to transmit light or by changing to another technique, such as capacitance, for determining the separation of the two plates.
(19) Bartell, L. S.; Betts, J. F. *J. Phys. Chem.* **1960**, *64*, 1075-1076.
(20) Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 1670-1673.

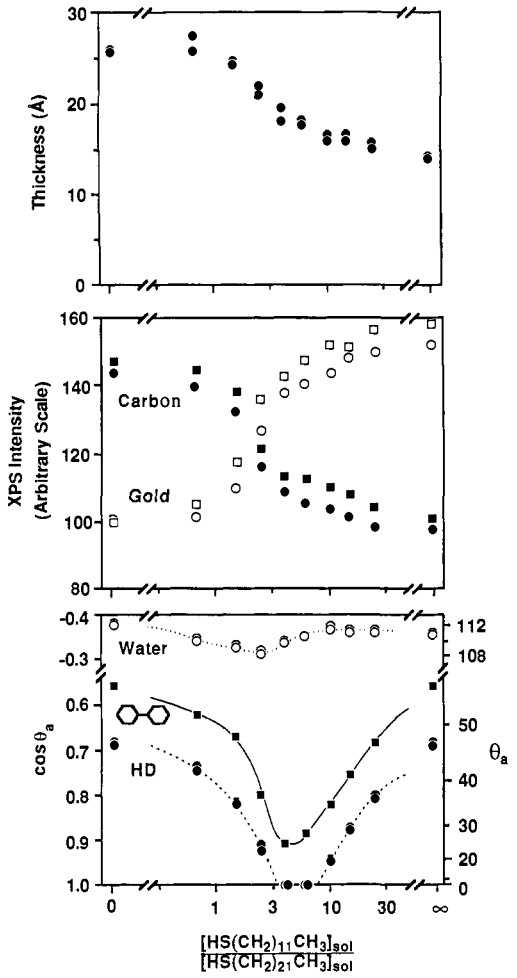

Figure 3. Monolayers adsorbed onto gold from mixed solutions of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ in isooctane. The abscissa represents the ratio of concentrations in solution on a logarithmic scale. Upper figure: ellipsometric thickness. Middle figure: intensity of the C(1s) (filled symbols) and $Au(4f_{7/2})$ photoelectron peaks (open symbols) in XPS. The areas of the gold peaks have been rescaled for clarity of presentation. The squares and circles represent two separate series of samples. The samples within each series were loaded into the spectrometer simultaneously and run sequentially. Lower figure: advancing contact angles of water (open circles), bicyclohexyl (squares), and hexadecane (filled circles). The lines have been added as aids to the eye and have no theoretical significance.

were autophobic[21] and oleophobic: $\theta_a(HD) = 47°$ for $HS(CH_2)_{21}CH_3$ and $\theta_a(HD) = 46°$ for $HS(CH_2)_{11}CH_3$. The contact angles on the mixed monolayers were lower than on the pure monolayers and reached a minimum between $R = 10$ and $R = 30$. There was a strong preference for adsorption of the longer thiol. The minimum in the contact angle of hexadecane occurred at an ellipsometric thickness intermediate between the thicknesses of the two pure monolayers. The form of the plot of contact angles against R is consistent with our hypothesis that the two components in the monolayer do not phase-segregate into macroscopic islands (Figure 1); if they did, each of the islands would be oleophobic, and we would expect $\theta_a(HD)$ to be independent of the composition of the monolayer. The contact angles in Figure 2 were measured after the gold slides had been immersed in the adsorption solutions for 6 days. The contact angles were unchanged after the slides had been reimmersed in the adsorption solutions for an additional 3 weeks.

$HS(CH_2)_{21}CH_3$ + $HS(CH_2)_{11}CH_3$ Adsorbed from Isooctane. We would expect a smaller difference between the chemical potentials of a long- and a short-chained thiol in a hydrocarbon solvent than in alcohol. Consequently, if the preference for adsorption of the thiol with the longer chain is thermodynamic, then by changing the solvent from ethanol to isooctane, the preference for the longer chain should decrease. Mixtures of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ were adsorbed onto gold from isooctane. The chosen values of R were concentrated around the minimum in θ (a preliminary experiment was performed to locate the approximate position of this minimum). Figure 3 shows the ellipsometric thicknesses of the monolayers, the intensities of the C(1s) and $Au(4f_{7/2})$ photoelectron peaks in XPS, the advancing contact angles of water and hexadecane (measured after immersion of the gold slides in the adsorption solutions for 1 day), and the advancing contact angle of bicyclohexyl (measured after immersion for 10 days). We observed no significant change in the advancing contact angles of water and hexadecane between 1-day and 10-day immersion. The adsorption isotherm is consistent with thermodynamic control over adsorption. The midpoint in the ellipsometric thickness and in the XPS intensities—an approximate gauge of the midpoint in the composition of the monolayer—and the minimum in the contact angle of hexadecane moved to lower values of R, compared to the adsorptions performed in ethanol. We also note the unexpected observation that the minima in the advancing contact angles of water and hexadecane occurred at different values of R and that the minimum in the contact angle of hexadecane appeared to be deeper than in the corresponding experiment performed in ethanol (Figures 2, 3, and 6).[22] Over a narrow range of concentrations near $R = 5$, the monolayers were wetted by hexadecane but not by hydrocarbons with higher surface tensions, such as bicyclohexyl ($\gamma_{lv} = 32.4$ mN/m compared to 27.2 mN/m for hexadecane[23]). This observation is consistent with our picture of a liquidlike hydrocarbon surface near the minimum in the contact angle.

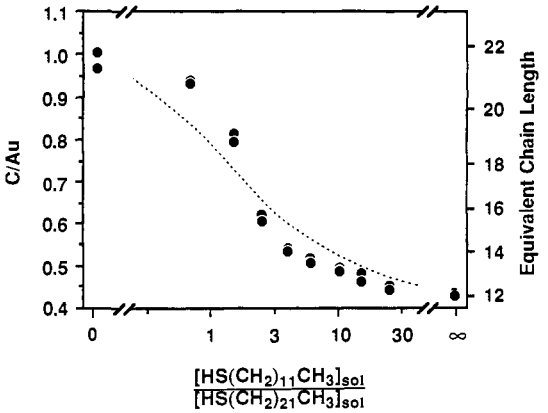

Figure 4. Ratio of C(1s) to $Au(4f_{7/2})$ peak areas in XPS for monolayers adsorbed onto gold from solutions of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ in isooctane. The right-hand axis shows the equivalent chain length, n, of a pure monolayer of $HS(CH_2)_{n-1}CH_3$, adsorbed from ethanol, that yields the same ratio of C/Au. The scatter in the data gives an indication of the random errors. The dotted line represents the ratio of C/Au peak areas expected theoretically if $[C_{22}]_{surf}[C_{12}]_{sol}/[C_{12}]_{surf}[C_{22}]_{sol} = 2.3$.

We determined the composition of the mixed monolayers by comparing the ratio of the intensities of the C(1s) and $Au(4f_{7/2})$ photoelectrons, obtained by XPS, with the ratios from monolayers of pure $HS(CH_2)_{n-1}CH_3$ (adsorbed from ethanol). Figure 4 shows the C/Au ratios calculated from the data in Figure 3, together with the equivalent chain lengths, n, of pure monolayers of alkanethiols. We assumed that $\chi^{C_{12}}$, the mole fraction of dodecanethiol in the monolayer, was linearly related to the equivalent chain length. We used the data from XPS rather than from ellipsometry to calculate the compositions because the data from XPS contained less scatter and yielded more precise compositions.[24] Figure 5 plots the advancing contact angles of water and

(21) A slide is autophobic if it emerges dry upon slow removal from the adsorption solution.

(22) From isooctane, wettable monolayers were formed over a range of R, from ethanol the minimum values of $\theta_a(HD)$ were 25° and 18° in two repetitions of the experiment.

(23) Jasper, J. J. *J. Phys. Chem. Ref. Data* **1972**, *1*, 841–1009.

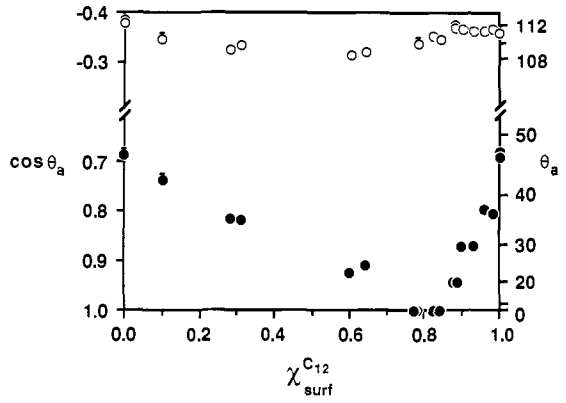

Figure 5. Advancing contact angles of water (open circles) and hexadecane (filled circles) plotted against the mole fraction of $HS(CH_2)_{11}CH_3$ in a monolayer adsorbed from mixtures of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ in isooctane. The mole fraction of $HS(CH_2)_{11}CH_3$ in the monolayer was calculated from the XPS data shown in Figure 4. The errors in the contact angles are within the symbols.

hexadecane against $\chi^{C_{12}}$ for mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{21}CH_3$ adsorbed from isooctane. The contact angle of water had a broad, shallow minimum near $\chi^{C_{12}} = 0.5$, whereas the contact angle of hexadecane reached a minimum around $\chi^{C_{12}} = 0.8$ (that is, when $[CH_3(CH_2)_{11}S]_{surf}/[CH_3(CH_2)_{21}S]_{surf} = 4$). The scatter in the data gives an indication of random errors.

Contact Angles of Dispersive Liquids on Mixed Monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_nCH_3$ Adsorbed from Ethanol. Theories of wetting, such as Fowkes' application of the geometric mean approximation (see below), seek to predict how the contact angles of liquids on dispersive surfaces vary with the surface tension of the liquid.[12] To test these theories, we measured the contact angles of four dispersive liquids (decane, hexadecane, bicyclohexyl, and α-bromonaphthalene) on mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{21}CH_3$ adsorbed from ethanol (Figure 6).[25] We chose decane as one of these liquids because its size matches the difference in chain lengths between the two adsorbates.[26] Bicyclohexyl and α-bromonaphthalene are liquids with high surface tensions that would be unable to penetrate into the cylindrical holes left by a molecule of dodecanethiol ($HS(CH_2)_{11}CH_3$) in a monolayer composed predominantly of docosanethiol ($HS(CH_2)_{21}CH_3$). These last two liquids did not wet any of the mixed methyl-terminated monolayers and hence gave information on interfacial free energies over the complete range of R.

Decreasing the difference in chain length between the two thiols resulted, as one would expect intuitively, in a shallower minimum in θ at a lower value of R. Figure 6 also shows the advancing contact angles on monolayers adsorbed from mixtures of $HS(CH_2)_{15}CH_3$ and $HS(CH_2)_{11}CH_3$ in ethanol, a difference of four carbons in the length of the chain.[27] The minimum in θ occurred near $R = 5$, compared to $R = 15$–30 for monolayers of $HS(CH_2)_{21}CH_3/HS(CH_2)_{11}CH_3$, in which the difference in chain length was 10 carbons.

Hysteresis on Mixed Methyl/Methylene Surfaces. Disorder in the outer part of the mixed monolayers would expose both terminal methyl groups and polymethylene chains at the surface. What effect would such microscopic heterogeneity have on the hysteresis in the contact angle? Figure 7 plots the hysteresis for mixed monolayers of $HS(CH_2)_nCH_3$ (n = 15, 21) and $HS(CH_2)_{11}CH_3$ adsorbed from ethanol and isooctane. Data were not included in these graphs if the receding contact angle was zero. The hysteresis in the contact angles of most hydrocarbons on the mixed monolayers was essentially independent of the composition of the monolayers.[28] The behavior of bicyclohexyl (BCH) differed slightly from the other hydrocarbons. On the mixed monolayers adsorbed from isooctane, the hysteresis in θ(BCH) was not correlated with the advancing contact angle but did show variations beyond the limits of experimental error. On the monolayer adsorbed from 30:1 $HS(CH_2)_{11}CH_3/HS(CH_2)_{21}CH_3$ in ethanol, the receding edge of a drop of bicyclohexyl tended to be pinned, and the resulting hysteresis was greater than on the other monolayers.

The advancing contact angle of water was very insensitive to the composition of the monolayer, but the hysteresis in the contact angle of water was greater on the mixed monolayers than on the pure monolayers for all the methyl-terminated systems studied.

$HS(CH_2)_{11}OH$ + $HS(CH_2)_{19}OH$ Adsorbed from Ethanol. In monolayers comprising mixtures of methyl-terminated thiols of different chain lengths, disorder in the outer part of the monolayer caused a decrease in the contact angle of hexadecane. Pure monolayers of $HS(CH_2)_{11}OH$ or $HS(CH_2)_{19}OH$ show wetting or near wetting behavior with water ($\theta_a(H_2O) < 10°$ and $<15°$, respectively). In monolayers comprising mixtures of these two thiols, disorder in the outer phase would expose nonpolar methylene groups at the surface and cause an increase in the contact angle

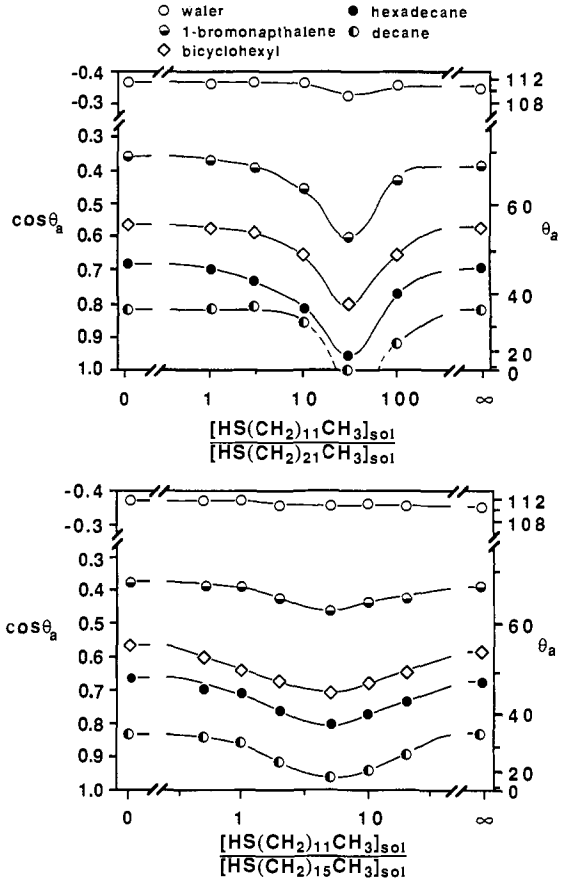

Figure 6. Advancing contact angles of water (○), α-bromonaphthalene (◒), bicyclohexyl (◇), hexadecane (●), and decane (◐) on mixed methyl-terminated monolayers adsorbed onto gold from ethanol. Upper figure: $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$. Lower figure: $HS(CH_2)_{15}CH_3$ and $HS(CH_2)_{11}CH_3$.

(24) After immersion for 1 day, the ellipsometric thicknesses yielded lower mole fractions of $HS(CH_2)_{11}CH_3$ in the monolayer than did the XPS data, due in large part to the anomalously low thicknesses[3] obtained for the pure monolayer of $HS(CH_2)_{21}CH_3$. After 10-day immersion, the agreement between the compositions calculated from XPS and ellipsometry was much better.

(25) In this experiment, the minimum in the contact angles occurred at a slightly different value of R compared to the experiment shown in Figure 2. This difference probably arises from inaccuracies in the preparation of the stock solution of $HS(CH_2)_{21}CH_3$.

(26) Nonane would actually fit better than decane in holes in the mixed monolayer, but the surface tension of nonane is inconveniently low.

(27) The ellipsometric thickness varied smoothly with composition.[5] The minimum in θ occurred at an ellipsometric thickness corresponding to $\chi \approx 0.6 \pm 0.2$, the large estimate of the limits of error arising from the small difference in thickness between the pure monolayers.

(28) α-Bromonaphthalene appeared slowly to cause damage to the thinner monolayers. As a result, the hysteresis in the contact angle increased gradually from 0.16 on the monolayer of $HS(CH_2)_{21}CH_3$ to 0.21 on the monolayer of $HS(CH_2)_{11}CH_3$. The hysteresis was not correlated with the contact angle itself: no increase in hysteresis was observed on the monolayers near the minimum in the contact angle.

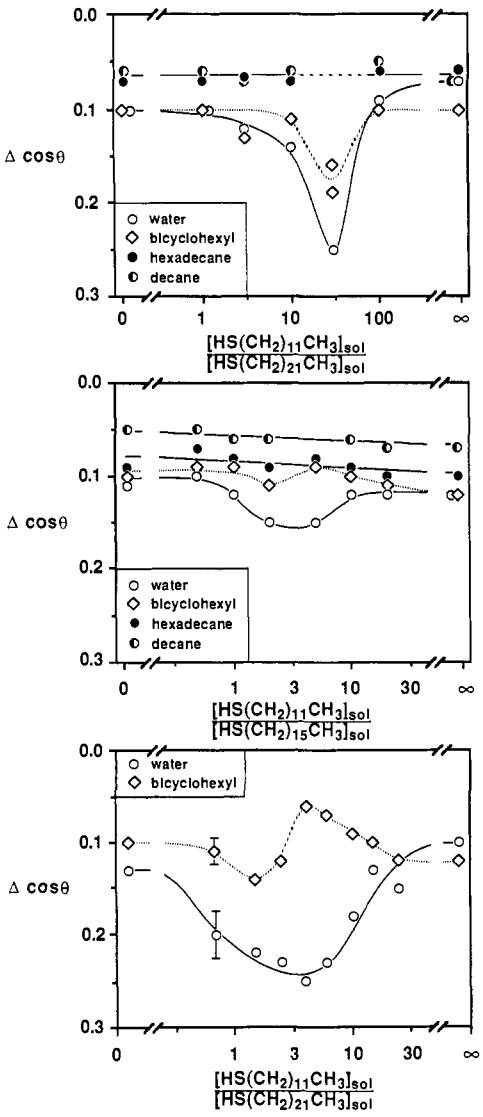

Figure 7. Hysteresis in the contact angles on mixed methyl-terminated monolayers on gold. Upper figure: $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ adsorbed from ethanol. Middle figure: $HS(CH_2)_{15}CH_3$ and $HS(CH_2)_{11}CH_3$ adsorbed from ethanol. Lower figure: $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ adsorbed from isooctane. $\Delta \cos\theta$ = cosine of the minimum receding contact angle minus cosine of the advancing contact angle. Lines have been added to these graphs purely as aids to the eye. The apparent variation in the hysteresis in the contact angle of bicyclohexyl in the middle figure may simply arise from random errors. Estimated limits of error are shown in the lower figure.

of water. Figure 8 plots the ellipsometric thickness and the advancing contact angle of water for mixed monolayers of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{19}OH$.[7] The contact angle showed a pronounced maximum, supporting our model of a disordered outer phase in the monolayer and militating against the formation of macroscopic, single-component domains. Figure 9 plots the contact angles of water against the composition of the monolayer, calculated on the assumption that the ellipsometric thickness (Figure 8) was a linear function of the mole fraction of the shorter thiol in the monolayer, $\chi^{C_{11}}{}_{surf}$. The standard errors shown were estimated from the distribution of the differences between the measured thicknesses of the monolayers on the two slides in each solution. The maximum in θ occurred at $\chi^{C_{11}}{}_{surf}$ = 0.5–0.6. The position of the maximum in θ is reasonable: at lower R, a large proportion of the surface comprises the hydroxyl termini of the long chains, whereas at higher R there are too few hydrocarbon chains to shield effectively the hydroxyl termini of the short chains from the molecules in the water drop. At the time these measurements were made, the monolayers had not fully reached equilibrium. Over a period of several weeks, the position of the

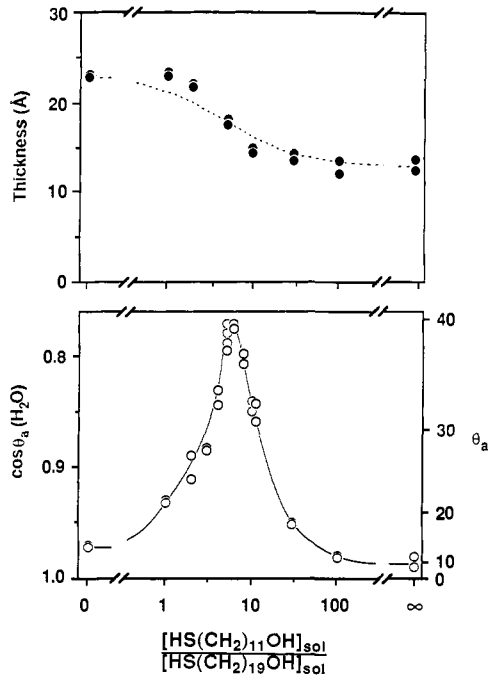

Figure 8. Mixed monolayers of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{19}OH$ adsorbed onto gold from ethanol: ellipsometric thickness (upper figure) and advancing contact angles of water (lower figure) as a function of the concentrations in solution. The lower figure includes additional data, in the region of the peak maximum, that are not shown in the upper figure. The dotted line in the upper figure represents the thickness expected theoretically if $[C_{19}]_{surf}[C_{11}]_{sol}/[C_{11}]_{surf}[C_{19}]_{sol} = 5$. The solid line in the lower figure is included as an aid to the eye.

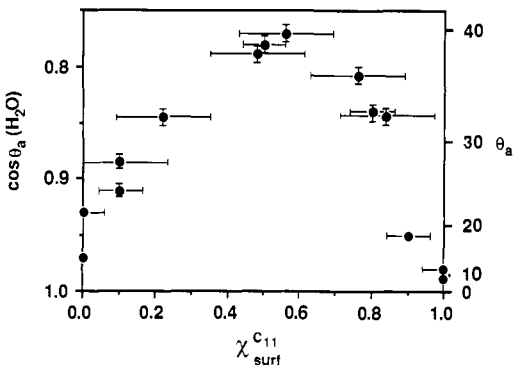

Figure 9. Advancing contact angles of water on mixed monolayers of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{19}OH$ on gold, plotted against the mole fraction of $HS(CH_2)_{11}OH$ in the monolayer. The composition of the monolayer was calculated from the ellipsometric thicknesses. The standard error bars were estimated from the differences in ellipsometric thickness between the monolayers on pairs of gold slides immersed in the same solutions.

maximum in the contact angle increased from $R = 6$ to $R \approx 11$.

$HS(CH_2)_{11}OH$ + $HS(CH_2)_{21}CH_3$ Adsorbed from Ethanol. Although the previous experiments confirm that macroscopic islands ($\gtrsim$0.1 μm, vide infra) do not form in the monolayers, the degree to which small aggregates or clusters of molecules of one species occur is unclear. One system in which the contact angles should be sensitive to the distribution of the components on a molecular length scale comprises mixed monolayers of a short hydroxyl-terminated thiol and a longer methyl-terminated thiol. If the two components are randomly mixed, then at low values of R the hydrocarbon chains of the methyl-terminated component will screen the hydroxyl groups from the contacting liquid.[29,30]

(29) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365–385.
(30) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897–5898.

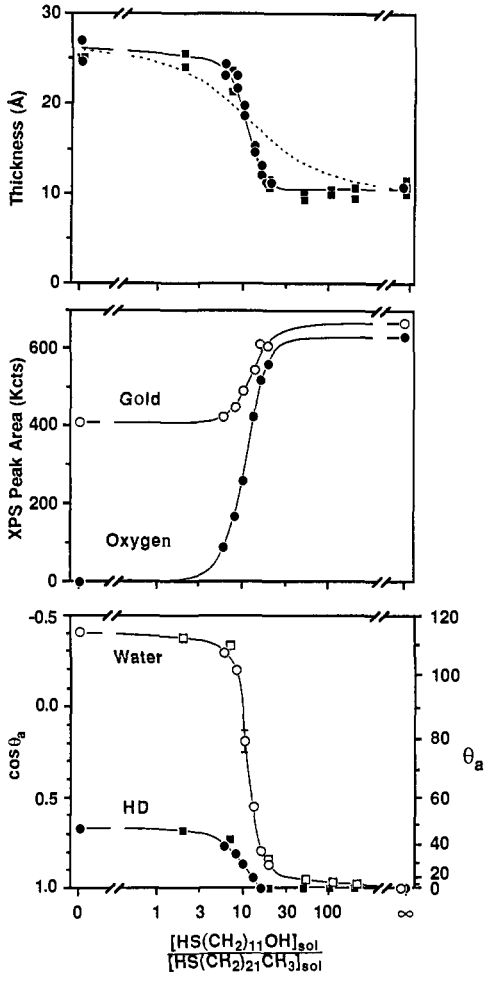

Figure 10. Competitive adsorption of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{21}CH_3$ from solution in ethanol onto gold. Squares and circles represent two separate experiments. Upper figure: ellipsometric thickness. The dotted line represents the thickness expected theoretically, using the experimental thicknesses for the pure monolayers, if $[C_{22}]_{surf}[C_{11}]_{sol}/[C_{11}]_{surf}[C_{22}]_{sol} = 11$. Middle figure: areas of the O(1s) and $Au(4f_{7/2})$ peaks in the XPS spectra. Lower figure: advancing contact angles of water and hexadecane. Each symbol represents two data points. With one exception, the variation in contact angle lay within the size of the symbol on the graph: an error bar is shown to indicate the difference in contact angles for the single exception.

If even small clusters of hydroxyl groups form, they will be accessible to a polar liquid.

Figure 10 plots the ellipsometric thickness, XPS intensities, and advancing contact angles of water and hexadecane, measured after overnight immersion, against the ratio of the two components in solution. All the experimental quantities measured showed a dramatic change over a narrow range in composition, $R = 7$–20. As with the monolayers comprising two hydroxyl-terminated thiols, these monolayers had not reached their limiting composition when the measurements were made. Figure 11 shows contact angles measured after reimmersion of the gold slides in the adsorption solutions for an additional 9 days. The advancing contact angles of water (filled circles) suggest that the midpoint in the composition had moved from $R = 11$ to $R \approx 14$ over the previous 9 days. The values of $\theta_a(H_2O)$ measured after overnight immersion are shown by the solid line. The solid bars indicate the values of the maximum advancing[31] and the minimum receding contact angles

(31) This system is the only one in which we observed large differences between the advancing and maximum advancing contact angles. For hydrocarbons on mixed methyl-terminated monolayers, the difference was less than 2°. The maximum advancing contact angle of water on the mixed methyl-terminated monolayers adsorbed from isooctane was ~115°, independent of composition. Sample contact angles on the mixed hydroxyl-terminated monolayers suggested that the difference between advancing and maximum advancing contact angles in that system was <5°.

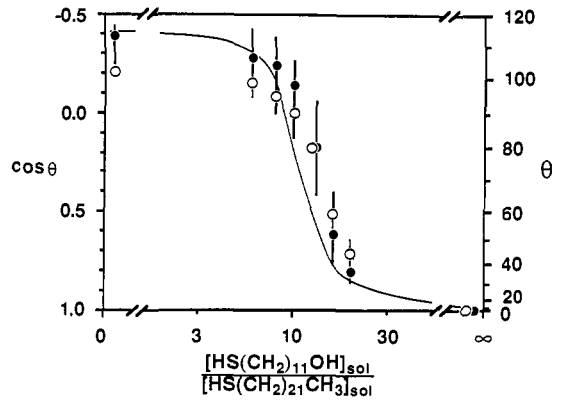

Figure 11. Contact angles on mixed monolayers of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{21}CH_3$ measured after immersion of the gold slides in the adsorption solutions for 10 days. The filled circles represent the advancing contact angles of water measured by forming a drop at the end of a needle, lowering the drop to the surface, and removing the needle. The solid line shows the values of the advancing contact angle of water on the same slides after they had only been immersed in the adsorption solutions overnight (from Figure 10). The solid bars indicate the values of the maximum advancing and minimum receding contact angles of water, measured by the technique of Dettre and Johnson.[51] The open circles represent the advancing contact angles of glycerol, also measured after 10 days. Glycerol was used to probe the accessibility of the hydroxyl groups to an H-bonding liquid that is more sterically hindered than water. The drops of glycerol were left for several minutes on the surface before the contact angles were measured to ensure that the limiting contact angles had been reached.

of water. We observed large hysteresis in the contact angles on the mixed monolayers. Figure 11 also shows the advancing contact angles of glycerol on the monolayers formed after 10-day immersion. Glycerol is a highly polar molecule but is bulkier and more sterically hindered than water and hence less able to reach and form hydrogen bonds to hydroxyl groups buried within a monolayer composed largely of docosane thiol moieties.

Discussion

Preferential adsorption of longer chains supports thermodynamic control over the adsorption process. Thermodynamically, cohesive interactions between hydrocarbon chains favor adsorption of the longer chains. As the difference in chain length increased (Figure 6), so did the preference for adsorption of the longer chain. It is difficult to conceive of an adsorption mechanism that would lead to a *kinetic* preference for the longer chain. The reactivity of the thiol group is the same for all the adsorbates. Diffusion favors the shorter thiol: the adsorbates in solution were monomeric,[32] and the methyl-terminated thiols do not have strongly bound solvation shells that could affect diffusion rates. Steric constraints to adsorption should increase with increasing chain length. Thus, we would expect the kinetics to favor adsorption of the shorter chain, contrary to experiment.

Furthermore, the adsorption isotherms of mixtures of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{21}CH_3$ in ethanol and isooctane were very different. There is no obvious kinetic rationale for such a large influence of the solvent. Thermodynamically, the greater preference for adsorption of the longer chain from ethanol is a direct consequence of the poorer solvation of hydrocarbon chains in ethanol compared to isooctane (vide infra).

Although the preference for the adsorption of the longer chain is most easily reconciled with predominantly thermodynamic control over the composition of the monolayer, there were indications of a kinetic component in the compositions of some of the monolayers (Figure 11). The slow change in some systems with time—involving incorporation of more of the long-chain component—suggests that the composition "frozen in" after the

(32) Costas, M.; Patterson, D. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 635–654.

presumptive initial equilibration was partially influenced kinetically by the large excess of the shorter chain in solution. The mechanism of this initial, rapid equilibration remains unclear. The slow progress toward the equilibrium composition is consistent with the rates of displacement of the components in fully formed monolayers by thiols in solution.[6] It is not clear why the monolayers that contained hydroxyl groups showed time-dependent behavior whereas the methyl-terminated systems reached their limiting properties upon overnight immersion.

The relationship between the composition of the monolayer and the composition of the solution can be rationalized in terms of the relative solubilities of the two components and the excess free energies of mixing in the solution and in the monolayer. In all the systems studied, adsorption of the longer chain was preferred over the shorter chain. The extent of the preference varied with the difference in chain lengths, the solvent, and the tail groups.

In the mixed Me/Me monolayers, the preference for adsorption of the longer chain can be understood intuitively on thermodynamic grounds if one recognizes that, to a first approximation, the activity of a thiol in a monolayer is similar to that in a crystal, with a constant additional term to account for the interaction with the gold. The component with the lower solubility, that is, the longer chain, will have a higher activity in solution and hence will be preferentially adsorbed into the monolayer. A similar argument holds for mixed monolayers of the two hydroxyl-terminated thiols. Where the tail groups are different, the nature of the solvent influences both the relative solubilities and the relative activities of the two components in the monolayer: preferential adsorption varies with the choice of solvent.[6]

The relationship between the concentrations of the two components in the monolayer and in solution was nonideal. We define a quantity K_{eq} by eq 2 where [long] and [short] are the concen-

$$K_{eq} = \frac{[\text{long}]_{surf}[\text{short}]_{sol}}{[\text{long}]_{sol}[\text{short}]_{surf}} \quad (2)$$

trations of the longer and the shorter of the two thiols in solution or thiolates on the surface. In Figures 4, 8, and 10, the dotted line indicates the XPS intensities or ellipsometric thicknesses that would be expected if K_{eq} were a constant given by the value of R for which $[\text{long}]_{surf} = [\text{short}]_{surf}$. The solutions used in these experiments were sufficiently dilute that we may assume that the activity coefficients in solution were constant. K_{eq} would thus be independent of concentration if the components in the monolayer also behaved ideally. In each case, the change in the composition of the monolayer with R was much sharper than would be expected if the monolayer were to act as an ideal two-dimensional solution. By analogy with nonideal solutions in three dimensions,[33] these adsorption isotherms could arise from a positive excess free energy of mixing of the two components in the monolayer. A positive free energy of mixing would disfavor monolayers containing a mixture of the two components with respect to monolayers composed largely of one component.

The composition of the monolayer and the distribution of the two components within the monolayer are determined by an interplay of enthalpic terms, which favor self-association of the components within a mixed monolayer, and entropic terms, which drive the formation of mixed monolayers containing two dispersed components. Disruption of the cohesive interactions between pseudocrystalline hydrocarbon chains in a pure monolayer or the breaking of hydrogen bonds between hydroxyl groups would both contribute to a positive enthalpy of mixing. The entropy of mixing can be broken down into three principal components: an ideal combinatorial term of the form $\sum \chi_i \ln \chi_i$, a positive excess term arising from the additional conformations available to the polymethylene chains in a disordered, liquidlike phase compared to the crystalline environment experienced in the pure monolayers, and a negative excess term arising from self-association of the components in the monolayer.

This balance of forces is most evident in the mixed monolayers derived from $HS(CH_2)_{11}OH$ and $HS(CH_2)_{21}CH_3$, which showed an abrupt transition between the two essentially pure monolayers. The energy required to isolate hydroxyl groups in the nonpolar environment provided by the alkyl chains of the longer, methyl-terminated thiol would be comparable to the strength of a hydrogen bond—~5 kcal/mol of hydroxyl groups. If the hydroxyl-terminated thiols were to form small, internally H-bonded clusters (analogous to those in alkane solvents[32]) to reduce the unfavorable enthalpy of mixing, the entropy of mixing would also be reduced. In either case, the transition from a pure monolayer of $HS(CH_2)_{21}CH_3$ to a monolayer composed largely of $HS(CH_2)_{11}OH$ would be much sharper than predicted for an ideal two-dimensional solution. For comparison, in solutions of alcohols in alkane solvents, both the enthalpy and the excess free energy of mixing are large and positive.[34]

Comparison of excess free energies of mixing also sheds light on the differences between mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{21}CH_3$ adsorbed from ethanol and isooctane. The enthalpy of mixing of liquid, linear alkanes and isooctane is positive, but the excess free energy of mixing is small and probably negative.[35] On the other hand, the excess free energy of mixing of alcohols and alkanes is large and positive, due to disruption of hydrogen bonds between alcohols, and orientation of molecules to avoid hydrophobic contacts.[36] Consequently, the difference between the chemical potentials of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ is likely to be much higher in ethanol than in isooctane, resulting in a greater preference for adsorption of the longer chain from ethanol than from isooctane. The greater depth of the minimum in θ_a(HD) observed in monolayers adsorbed from isooctane than from ethanol can also be rationalized on thermodynamic grounds. We believe that changes in θ_a(HD) in this system reflect changes in the extent of disorder in the surface of the monolayer. In isooctane, entropy would tend to drive the outer part of the monolayer toward the most chaotic, liquidlike state. In ethanol, the positive enthalpy of mixing and negative excess entropy of mixing of the solvent and the alkyl chains would both favor dense clusters of the alkyl chains.[37]

Mixed monolayers do not phase-separate into macroscopic islands. The pronounced minima in the contact angles of hexadecane on mixed methyl-terminated monolayers is strong evidence against the formation of large, single-component domains. If islands more than a few tens of angstroms across were predominant on the surface, the wetting properties of the monolayer would be determined by molecules within the islands and not by those at the domain boundaries. Since the methyl groups in each island would be expected to be ordered and well-packed, the mixed monolayers would exhibit the wetting properties of the pure monolayers, i.e., the mixed monolayers would be oleophobic (Figure 1).

A similar argument applies to the mixed monolayers of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{19}OH$. The maximum contact angle of water was similar to that observed on a well-packed monolayer composed of ~60% hydroxyl- and 40% methyl-terminated thiols of the same length.[6,38] If we assume that the mixed OH/OH monolayer with the highest contact angle ($\chi^{C_{11}}_{surf} = 0.6$) exposes 60% hydroxyl groups and 40% methylene chains at the surface, then it is implausible that single-component clusters could be more than ~10–20 Å across.

(33) Rowlinson, J. S. *Liquids and Liquid Mixtures*; Butterworth: London, 1969; Chapters 4 and 5.

(34) Reference 33, pp 162–165.

(35) Larkin, J. A.; Fenby, D. V.; Gilman, T. S.; Scott, R. L. *J. Phys. Chem.* **1966**, *70*, 1959–1963. McGlashan, M. L.; Morcom, K. W.; Williamson, A. G. *Trans. Faraday Soc.* **1961**, *57*, 601–610.

(36) Brown, I.; Fock, W.; Smith, F. *Aust. J. Chem.* **1964**, *17*, 1106–1118.

(37) This clustering would have to arise from a different distribution of the components in the monolayer, not merely from differences in the structure of the outer phase of the monolayer: reconstruction of the fluid outer phase upon removing the monolayer from solution is probably very rapid. The differences observed between monolayers with the same average composition suggests that lateral mobility in fully formed monolayers is low. If lateral mobility were high, all the monolayers would reconstruct to the same structure in the time it took to measure contact angles.

(38) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 6560–6561.

The next question is to what extent is the distribution of the components in the monolayer nonstatistical? Both combinatorial and conformational entropy favor dispersion of the two components, but cohesive interactions between hydrocarbon chains or hydrogen bonds between hydroxyl groups favor self-association. A balance between these two opposing forces will, in general, result in a nonrandom distribution of the components within the monolayer. For mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{21}CH_3$, we might expect the most oleophilic monolayer to be the maximally mixed monolayer; that is, the minimum in θ(HD) would occur at $\chi^{C_{12}} = 0.5$. For monolayers adsorbed from isooctane, the minimum occurred around $\chi^{C_{12}} = 0.8$, suggesting that there may be some clustering in the outer part of the monolayer at lower concentrations. The apparent difference in the depth of the minima in θ(HD) on the monolayers adsorbed from ethanol and isooctane may also have arisen from variations in the distribution of the components of the monolayer on a molecular length scale. On the other hand, the anomalous behavior of the contact angles of decane on mixed monolayers of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ at low $\chi^{C_{12}}$ (vide infra) requires that the $HS(CH_2)_{11}CH_3$ moieties be isolated in the monolayer: if they were clustered, selective interactions with decane would not occur.

The contact angles on mixed monolayers of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{21}CH_3$ suggest that the hydroxyl-terminated thiol may aggregate into small clusters when it is the minor component in the monolayer. Of all the monolayers presented in this study, the mixed monolayers of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{21}CH_3$ showed the most dramatic variations in composition and contact angles with the composition of the solution. Over the narrow range of $R = 7$–20, the composition of the monolayer changed from almost exclusively $HS(CH_2)_{21}CH_3$ to largely $HS(CH_2)_{11}OH$ with only a few pendant chains of $HS(CH_2)_{21}CH_3$ extending above the surface. The energy required to disperse hydroxyl groups in a nonpolar environment is very high: in mixtures of alcohols and alkanes in solution, the alcohols are aggregated, largely as tetramers, even at very low mole fractions ($\chi^{OH} \approx 0.01$).[32] By analogy, in monolayers in which the hydroxyl-terminated thiol is the minor component, the alcohol groups are probably arranged in small, internally H-bonded clusters. A detailed analysis[5] of contact angles supports this model: at low χ^{OH}, the hydroxyl groups were still accessible to water and glycerol but did not appear to influence the contact angle with hexadecane. By comparison, the carboxylic acid groups in a monolayer of the unsymmetrical sulfide, $CH_3(CH_2)_{21}S(CH_2)_{10}CO_2H$, on gold are completely shielded from a water drop by a sea of hydrocarbon chains.[29] In monolayers composed largely of the hydroxyl-terminated thiol, the absence of cohesive interactions between hydrocarbon chains, which favor adsorption of the longer chain at lower R, resulted in little incorporation of $HS(CH_2)_{21}CH_3$ into the monolayer.[39]

A full understanding of the contact angles on mixed methyl/methylene surfaces probably requires consideration of the microscopic roughness of the surface and the entropy of mixing at the monolayer–liquid interface, in addition to dispersive interactions between the phases.

(1) Geometric Mean Approximation. Our model of mixed monolayers of methyl-terminated thiols with different chain lengths is an oriented, densely packed inner phase surmounted by a disordered, liquidlike outer phase. The interaction of the monolayer with a supernatant liquid is purely dispersive through interactions with the methyl groups and polymethylene chains—the underlying gold substrate is prevented from interacting with the liquid by the thickness of the dense inner phase. Fowkes has proposed a theoretical model[12] for evaluating contact angles at interfaces in which the interaction between the two phases is dominated by dispersion forces. His approach assumes that the liquid and solid interact enthalpically purely through van der Waals interactions. Fowkes used the geometric mean approximation to express the solid–liquid free energy in terms of the liquid–vapor and solid–vapor free energies: for a purely dispersive system,

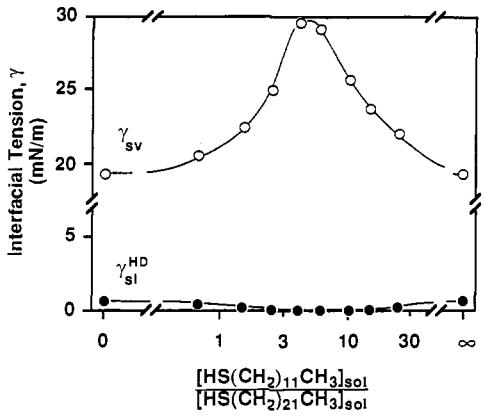

Figure 12. Interfacial tensions of mixed monolayers of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ adsorbed from isooctane, calculated by using the geometric mean approximation. Filled symbols: interfacial tension between the surface and hexadecane. Open symbols: surface tension of monolayer calculated from the contact angles of bicyclohexyl ($R = 4, 6$) and hexadecane (other data points).

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2(\gamma_{sv}\gamma_{lv})^{1/2} \quad (3)$$

If γ_{sv} is known, then cos θ can be predicted from Young's equation[40]

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (4)$$

If γ_{sv} is unknown, the geometric mean approximation predicts that, for a range of liquids, cos θ should scale as $\gamma_{lv}^{-1/2}$. This theory only incorporates effects due to interfacial entropy that adhere at least approximately to the geometric mean combining rule.[41] The entropy of mixing at the monolayer–liquid interface cannot be predicted by such a theory since there is no contribution to γ_{sv} or γ_{lv} from the entropy of mixing. The contact angles of a series of structurally similar liquids with different surface tensions (e.g., *n*-alkanes or *n*-alcohols) on pure methyl surfaces follow the predictions of the geometric mean approximation.[3] The advancing contact angles on mixed monolayers of $HS(CH_2)_{11}CH_3/HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3/HS(CH_2)_{15}CH_3$ were also self-consistent within the theory, with the exception of the contact angles of water in both systems and the contact angles of decane on the C_{22}/C_{12} monolayers (Figure 6). We used the geometric mean approximation and the advancing contact angles of hexadecane (or bicyclohexyl for the monolayers that were wet by hexadecane) to calculate γ_{sv} and γ^{HD}_{sl} on mixed monolayers of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ adsorbed from isooctane (Figure 12). One of the corollaries of the geometric mean approximation is that, for the systems studied here, changes in the contact angle are dominated by changes in γ_{sv}, not γ_{sl}. Hexadecane, bicyclohexyl, and α-bromonaphthalene have different molecular shapes and might be expected to interact differently with the surface of the monolayer. Within the geometric mean approximation, γ_{sl} is small and always positive. Since specific interactions can only perturb γ_{sl}, such effects should not have a major influence on the measured contact angle.

(2) Extensions to the Theory of Fowkes. The theory of Fowkes makes two implicit assumptions that are almost certainly untrue for the systems studied here. The first is that the surfaces of the monolayers are planar and hence that changes in the surface tension of the solid derive from changes in the polarizability of

(39) At sufficiently low concentrations of one component in the monolayer, the combinatorial entropy of mixing (which scales as $\chi \ln \chi$) dominates enthalpic terms (which scale as χ). The contact angles of water suggest that even at $R = 200$ some small amount of $HS(CH_2)_{21}CH_3$ was incorporated into the monolayer.

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

(41) Good, R. J. *J. Phys. Chem.* **1957**, *61*, 810–813. Fowkes, F. M. In *Surfaces and Interfaces, I—Chemical and Physical Characteristics*; Burke, J. J., Reed, N. L., Weiss, V., Eds.; Syracuse University Press: Syracuse, NY, 1967.

the surface. The second is that the interfacial entropy scales with the enthalpy and hence that there is no entropy of mixing at the solid–liquid interface.

One alternative perspective on γ_{sv}, which may be more useful in understanding the systems in this paper, is to regard the interfacial tension as fixed (since methyl and methylene groups have comparable volume polarizabilities[42]) and allow the area of the exposed molecular surface to vary by incorporating a roughness factor, r. In disordered, liquidlike monolayers, we would expect the area of the exposed van der Waals surface to be greater than in an ordered, densely packed methyl surface and the value of r to be correspondingly higher. The higher the value of r, the lower the contact angle.[43] If we then apply the geometric mean approximation to the true interfacial tension, we obtain the same $\gamma_{lv}^{-1/2}$ functional dependence of cos θ.

This alternative approach still does not account specifically for interfacial entropy. There are two contributions to the entropy of the solid–liquid interface that might be expected to influence the contact angles. For hexadecane on pure methyl-terminated monolayers, the interfacial entropy is probably small. On a mixed monolayer, the hexadecane dissolves in the liquidlike outer part of the monolayer, giving rise to a combinatorial contribution to the entropy. An increase in the number of conformations energetically accessible to the chains on the surface increases the conformational entropy of the interface. These entropic contributions could be of comparable size to the observed changes in surface free energies: for example, $N_A k \ln 2$ (the molar entropy of mixing of equal quantities of two ideal liquids) converts to a surface free energy of 14 mN/m at room temperature. If the entropy of mixing is important, then, contrary to the model of Fowkes, changes in γ_{sl} play a major role in determining changes in the contact angle.[44] A corollary of including entropy terms in γ_{sl} is that γ_{sl} would become negative on many of the mixed monolayers.[45]

(3) Shape-Selective Interaction between the Monolayer and the Solvent. The shape of the decane molecule approximately matches the vacancies created in a monolayer of $HS(CH_2)_{21}CH_3$ by the incorporation of $HS(CH_2)_{11}CH_3$. If molecules of decane were to fill in these holes, the resulting surface would approximate a pure methyl surface. On mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{15}CH_3$ (Figure 6), the contact angles of decane followed the pattern expected on the basis of the contact angles of hexadecane and the respective surface tensions. On mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{21}CH_3$, however, the contact angles of decane deviated markedly from the prediction of the geometric mean approximation. As R increased and θ_a(HD) decreased, the contact angle of decane initially did not change (Figure 6). This behavior is shown graphically in Figure 13, which plots {cos θ(decane(R)) − cos θ(decane(R = 0))} against the corresponding change in the contact angles of hexadecane. The

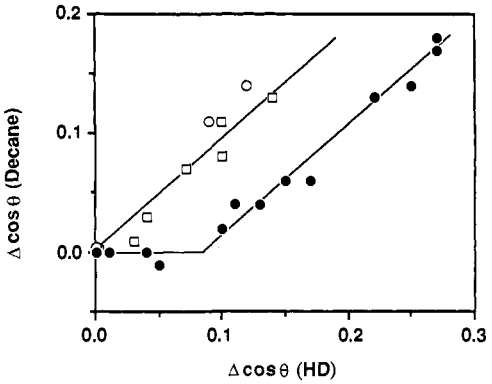

Figure 13. Changes in the advancing contact angles of decane and hexadecane on mixed monolayers of methyl-terminated alkanethiols. $\Delta \cos \theta$ = (cos θ at composition R) − (cos θ at R = 0). Filled circles represent data for monolayers adsorbed from mixed solutions of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{21}CH_3$ in ethanol and isooctane, in which the contact angles were decreasing with increasing ratio of $HS(CH_2)_{11}CH_3$ to $HS(CH_2)_{21}CH_3$ in solution. Open circles represent monolayers from the same systems in which the contact angle was increasing with increasing ratio of $HS(CH_2)_{11}CH_3$ to $HS(CH_2)_{21}CH_3$ in solution. There are very few data in this range because the contact angle of decane was zero on most of these monolayers. The open squares represent monolayers adsorbed from mixed solutions of $HS(CH_2)_{15}CH_3$ and $HS(CH_2)_{11}CH_3$ in ethanol. There was no experimental difference between the two concentration regimes for this system.

filled circles represent data obtained when R was less than the value that yielded the minimum in the contact angle of hexadecane and were derived from several experiments. Data with R greater than this minimum point are shown by open circles. For most data in this regime, the contact angle of decane was zero, and these points are not included in the figure: the two remaining data points fall on the same line as the data from the mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{15}CH_3$ (open squares) and are broadly in accord with the geometric mean approximation for γ_{sl}. The data represented by solid circles can be described by two intersecting straight lines. At low R, θ_a(decane) did not change with decreasing θ_a(HD). Once about 20% of the monolayer was composed of $HS(CH_2)_{11}CH_3$ moieties, θ_a(decane) started to decrease: at higher R, the data followed a straight line parallel to the open symbols. The anomalous behavior of the contact angle of decane on monolayers of $HS(CH_2)_{21}CH_3$ admixed with some $HS(CH_2)_{11}CH_3$ suggests that decane was able to intercalate into voids in the monolayer. The resulting monolayers would be densely packed and would present a surface comprised essentially of methyl groups.

(4) Reasons Why the Contact Angles of Decane and Water Might Deviate from the Theory of Fowkes. If the molecules of decane only intercalate into the monolayer at the monolayer–liquid interface, then, within the geometric mean approximation, the effect on the contact angle of incorporating decane into the mixed monolayer should be minimal, since $\gamma_{sl} \approx 0$ for decane on both a pure methyl and a disordered methyl/methylene surface. In order to explain the observed plateau in θ(HD) at low R, the decane would also have to penetrate into voids at the monolayer–vapor interface. The contact angles of decane were measured under dry spreading conditions, so it is unlikely that the decane was incorporated into the monolayer before the drop was placed on the surface.[46] There are two plausible explanations. First, molecules of decane in a thin precursor film[14] advancing in front of the drop could penetrate into holes in the monolayer, with the energy of this process being dispersed in the advancing film. Second, the entropy of mixing may play an important role in lowering γ_{sl} in the mixed monolayers. If molecules of decane plug the holes in the monolayers of $HS(CH_2)_{21}CH_3$ and are integrated into the monolayer, then there is no entropy of mixing between

(42) The molecular polarizability of a linear alkane with n carbons is given approximately by $10^{24}\alpha = 4.6 + 1.8(n-2)$ cm^3. After compensation for the different molar volumes, the polarizability of a methyl and a methylene group are comparable (Hill, N. E.; Vaughan, W. E.; Price, A. H.; Davies, M. *Dielectric Properties and Molecular Behavior*; Van Nostrand Reinhold: London, 1969; p 192).

(43) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988–994.

(44) A positive term due to ΔH^{mix} also contributes to the interfacial tension. For hydrocarbons on hydrocarbon surfaces, ΔH^{mix} is likely to be much smaller than ΔS^{mix}.

(45) One way of testing the hypothesis that part of the changes observed in the contact angles on mixed methyl/methylene surfaces is due to the entropy of mixing is to measure the contact angles with a dispersive liquid that is immiscible with hydrocarbons. The closest we could approach this experiment was to measure contact angles with perfluorodecalin. The free energy of mixing of fluorocarbons and hydrocarbons is much lower (i.e., less negative) than of two hydrocarbons. For example, the consolute temperature of heptane/fluoroheptane mixtures is 50 °C (Scott, R. L. *J. Phys. Chem.* **1958**, *62*, 136–145). The results of this experiment were inconclusive. We note that the geometric mean approximation predicts that perfluorodecalin (γ_{lv} = 18.3 mN/m) should wet even a pure methyl-terminated monolayer (γ_{sv} = 19.3 mN/m).[3] The advancing contact angle of perfluorodecalin on a monolayer of docosanethiol on gold was 39°, and the receding contact angle was 34°. The failure of the geometric mean approximation for fluorocarbon–hydrocarbon mixtures is well-known (Scott, R. L. op. cit.).

(46) The contact angle of hexadecane on the monolayer adsorbed from isooctane with R = 1.5 was unaffected by the presence of a partial pressure of decane vapor.

the densely packed mixed monolayer incorporating decane and the supernatant decane and hence no change in the *equilibrium* contact angle. The question of how the energy of reaction (for the insertion of molecules of decane into the monolayer) would be dissipated remains unclear.[47]

The advancing contact angle of water was remarkably insensitive to variations in the structure of the surfaces of the mixed monolayers of methyl-terminated thiols. Fowkes' theory, based on the assumption that the liquid and solid interact enthalpically through dispersive forces alone, predicts a maximum range of 9° in the contact angle of water[48] on the monolayers adsorbed from $HS(CH_2)_{11}CH_3/HS(CH_2)_{21}CH_3$ in isooctane, compared to the 3–4° range observed in the advancing contact angle. There are several ways of explaining this discrepancy. First, it might be an experimental artifact. The hysteresis in the contact angle of water was higher on the mixed surfaces than on the pure monolayers. Consequently, the true, equilibrium contact angle might follow the predicted behavior even though the advancing contact angle did not. Second, it might reflect microscopic roughness. Let us assume the measured contact angles are close to the thermodynamic values. Then an increase in γ_{sv} with increasing R must be matched by a corresponding *increase* in γ_{sl}. Such an increase could result from a greater area of (unfavorable) contact between the monolayer and water on mixed monolayers than on the pure monolayers. Third, it might arise from the entropy of mixing. Alkanes and water are immiscible. If the entropy of mixing is an important contributor to the decrease in the contact angles of hydrocarbons on the mixed monolayers, then a smaller change in θ should be observed with water since there is little entropy of mixing at the monolayer–water interface. The different positions of the minima in the contact angles on mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{21}CH_3$ (near $\chi^{C_{12}} = 0.5$ for water, $\chi^{C_{12}} = 0.8$ for hexadecane) demonstrate that the molecular interactions at the monolayer/water interface and the monolayer/hydrocarbon interface are different.

The hysteresis on mixed monolayers of methyl-terminated thiols is not consistent with models based on macroscopic heterogeneity. We observed some hysteresis in all the contact angles on the mixed methyl/methylene surfaces (Figure 7). For surfaces on which the receding angle was nonzero, the hysteresis with nonpolar liquids was, with a few exceptions, essentially constant, independent of the degree of disorder in the outer part of the monolayer film. The absolute size of the hysteresis of the dispersive liquids, expressed as cosines, increased with increasing surface tension. In contrast to the dispersive liquids, the advancing contact angle of water was relatively insensitive to the structure of the surface, but the hysteresis in the contact angle of water was greater on the mixed surfaces than on the pure methyl surfaces. Recalling the results from the companion paper,[6] we can summarize our observations on hysteresis as follows:

(i) On well-packed surfaces composed of polar and nonpolar components, the advancing contact angle of water is sensitive to the composition of the surface, but the hysteresis in the contact angle is constant.

(ii) On disordered surfaces comprised of methyl and methylene groups, the advancing contact angle of water is insensitive to the structure of the surface, but the hysteresis is greater on the disordered surfaces.

(iii) On disordered surfaces comprised of methyl and methylene groups, the advancing contact angles of dispersive liquids are very sensitive to the structure of the surface, but the hysteresis is approximately invariant.

Current theories of wetting explain hysteresis by roughness or heterogeneity on a macroscopic scale ($\gtrsim 0.1$ μm).[11] The mixed monolayers studied here are homogeneous on that length scale. It will be necessary to develop a microscopic theory to explain hysteresis in these systems.

Contact angles are more sensitive than optical ellipsometry or X-ray photoelectron spectroscopy to certain small structural changes in monolayers. In monolayers in which the two components have the same chain length but different tail groups, contact angles are sensitive to the composition so long as the wettability of the two tail groups is different but are in general a nonlinear function of the composition of the monolayer and cannot be used for quantitation. XPS provides a quantitative measure of the composition provided that at least one component produces a unique, resolvable photoelectron peak. The sensitivity of XPS is comparable to that of contact angles when the component carrying the XPS tag is at low concentration. At higher concentrations, the errors in the acquisition and processing of the XPS data reduce the accuracy of the compositions and hence the ability to discriminate between two monolayers that differ slightly in composition.[49] For most of the systems studied in the preceding paper, the sensitivity of the contact angle to changes in composition also decreased at high χ^P.

In monolayers containing two thiols with different chain lengths, the errors in XPS (particularly in the C/Au ratio) are less than in ellipsometry, allowing more precise calculations of compositions by XPS. Approximations are made in the analysis of the XPS data, however, which reduce the accuracy of the computed compositions. If one of the tail groups contains a heteroatom (or the tail groups contain different heteroatoms), the intensity of the photoelectrons from the heteroatom provides another estimate of composition. In these monolayers with mixed chain lengths, contact angles can detect subtle variations in the monolayer that are buried deep in the noise in ellipsometric measurements or X-ray photoelectron spectra. Two examples illustrate this point. The contact angle of hexadecane on monolayers adsorbed from a solution of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}CH_3$ in isooctane at $R = 100$ was 43° compared to 47° on the monolayer adsorbed from pure $HS(CH_2)_{11}CH_3$. At the same value of R, mixed monolayers of $HS(CH_2)_{21}CH_3$ and $HS(CH_2)_{11}OH$ yielded a contact angle of water of 14° compared to 7° on the pure hydroxyl-terminated monolayer. In neither case could we detect any significant difference by XPS or ellipsometry between the monolayers at $R = 100$ and $R = \infty$.

The contact angle of hexadecane is probably the most sensitive measure currently available of the quality of monolayers composed of methyl-terminated hydrocarbon chains.

Conclusions

(1) Mixed monolayers of thiols on gold containing two components of different chain length provide a convenient means of introducing disorder into interfaces. The degree of disorder may be controlled by varying the relative concentration of the two thiols in solution. The monolayer–liquid or monolayer–vapor interface is insulated from the influence of the underlying gold substrate by a layer of densely packed, ordered polymethylene chains. The structure of the interface can be varied further by changing the nature of the tail groups or by introducing functional groups into the hydrocarbon chains that form the backbone of the monolayer.

(2) The composition of monolayers adsorbed from solutions containing mixtures of thiols appears to be determined principally by thermodynamics, although the mechanism by which the components in the monolayer and in solution equilibrate remains unclear. Among the most compelling observations that militate against kinetic control over the adsorption process are the preferential adsorption of longer chains over shorter chains; the dramatic variation in the composition of the monolayer with the nature of the solvent, even when there are no specific interactions between the adsorbates and the solvent; and the strong preference

(47) It is not clear how best to incorporate the energy of reaction into the theory of reactive spreading. Experiments on the ionization of carboxylic acids at interfaces suggest that the energy of reaction may influence the contact angle in some systems but not in others: Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921–937. Reference 5.

(48) This value was calculated from the values of γ_{sv} in Figure 12, with $\gamma(H_2O) = 72$ mN/m and $\gamma^d(H_2O) = 21$ mN/m.

(49) Near-monolayer coverage of the molecule containing the elemental tag, the error in compositions calculated by XPS is ~5%. The lower limit on the concentration of a species that can be quantitated by XPS depends on the species being studied. For example, by tagging alcohols at the surface of a monolayer with trifluoroacetate groups, it should be possible to detect 1% of a monolayer of hydroxyl-terminated thiols.

for the adsorption of the minor component from a solution containing two structurally similar thiols ($HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{11}OH$ in isooctane).[50]

(3) The relationships between the compositions of monolayers and the solutions from which they are adsorbed are nonideal. Monolayers containing comparable amounts of the two components are disfavored relative to monolayers composed largely of a single component. The adsorption isotherms can be understood qualitatively on the assumption of thermodynamic equilibrium between the monolayer and the adsorption solution and consideration of excess enthalpies and entropies of mixing.

(4) The components in the monolayer do not phase-segregate into macroscopic islands. Any clusters that do form are no more than a few tens of angstroms across. It is unlikely, however, that the two components are randomly dispersed throughout the monolayer. There is some evidence for aggregation on a molecular length scale, but it is difficult to derive a detailed picture of the distribution of the two components in the monolayer.

(5) We attempted to model the wettability of the mixed monolayers of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_nCH_3$ by the approach of Fowkes, who employed the geometric mean approximation to estimate the solid–liquid interfacial free energy. Although reasonable agreement was found for hexadecane, bicyclohexyl, and α-bromonaphthalene, there were significant differences between the theoretical predictions and the observed contact angles of water and decane. Fowkes' model applies to planar interfaces in which there is no entropy of mixing between the solid and the liquid. We believe that a detailed model of the wettability of these mixed monolayers will have to incorporate entropy specifically. The relative importance of enthalpic and entropic terms and how best to incorporate entropy into a coherent theory remain unclear.

(6) The variation in hysteresis in the contact angle with the nature of the probe liquid and the structure of the monolayers cannot be explained on the basis of macroscopic heterogeneity, since no such heterogeneity exists in these systems. Hysteresis contains much information about the structure of the surface but, in the absence of a microscopic theory, can only be interpreted through comparison of a number of different systems.

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Registry No. HD, 544-76-3; Au, 7440-57-5; $HS(CH_2)_{21}CH_3$, 7773-83-3; $HS(CH_2)_{11}CH_3$, 112-55-0; $HS(CH_2)_{15}CH_3$, 2917-26-2; $HS(CH_2)_{11}OH$, 73768-94-2; $HS(CH_2)_{19}OH$, 114896-31-0; decane, 124-18-5; bicyclohexyl, 92-51-3; α-bromonaphthalene, 90-11-9.

(50) $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{11}OH$ have similar sizes, shapes, and polarizabilities. At low concentrations in isooctane, H bonding does not play an important role.

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Reversible Coordination and Facilitated Transport of Molecular Nitrogen in Poly((vinylcyclopentadienyl)manganese) Membrane

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Abstract: Kinetic and equilibrium constants of nitrogen coordination to cyclopentadienylmanganese (CpMn) are spectroscopically determined by using the membrane of the copolymer of (vinylmethylcyclopentadienyl)dicarbonylmanganese and octyl methacrylate. Nitrogen transport through the membrane is selectively augmented due to the rapid and reversible coordination of nitrogen to the fixed CpMn. The facilitated nitrogen-transport behavior is in accordance with a dual-mode transport model to give diffusion coefficients of the penetrant.

Much effort has been expended in studying the selective transport of gaseous molecules through polymeric membranes.[1] Recently we reported highly selective transport of molecular oxygen through polymer membranes containing a (porphinato)cobalt complex as the fixed carrier of oxygen.[2] The key experiment to establish the facilitated oxygen transport involved the proper preparation of a polymer (porphinato)cobalt membrane in which molecular oxygen coordinates to the complex rapidly and reversibly even in the solid state. The permeability ratio of oxygen against nitrogen was greater than 10 through the membrane containing a large amount of the (porphinato)cobalt. This membrane was successfully employed as an oxygen-enriching membrane to separate oxygen from air.[2]

A polymer containing the metal complex to which molecular nitrogen coordinates rapidly and reversibly is expected to transport nitrogen selectively and to show the possibility of a nitrogen-enriching membrane from air. A large number of transition-metal complexes of molecular nitrogen have been synthesized.[3] However, these studies are aimed at nitrogen fixation through the reduction of the nitrogen coordinated to a metal ion, and the nitrogen complexes themselves often undergo degradation under an air atmosphere. Therefore, kinetic and equilibrium profiles of the nitrogen coordination to the metal ion have been receiving surprisingly little attention.

We have reviewed the effects of a polymer matrix to reduce the degradation of a metal complex: an immobilization effect to inhibit a dimerization of metal complexes and an environmental effect to suppress a redox reaction of metal complexes.[4] Here we successfully prepared a transparent and flexible polymer

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