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ω-Terminated Alkanethiolate Monolayers on Surfaces of Copper, Silver, and Gold Have Similar Wettabilities[1]

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Abstract: Long-chain alkanethiols (HS(CH$_2$)$_n$X) adsorb from solution onto the surfaces of freshly evaporated copper, silver, and gold films and form oriented monolayers. Both polar and nonpolar tail groups (X) can be accommodated in these adsorptions. Adsorption on all three metals generates self-assembled monolayers (SAMs) exhibiting similar wetting properties. X-ray photoelectron spectrocopy (XPS) data suggest that the ω-terminated n-alkanethiolate monolayers, like those derived from simple alkanethiols, are composed of trans-extended chains having orientations on copper and silver that are closer to the perpendicular to the surface than are those on gold. These observations suggest that variations in the structure of the underlying polymethylene region of these SAMs have little effect on the interfacial free energy of the SAM as manifested by wetting. We have also characterized monolayers ("mixed monolayers") prepared by exposure of all three metals to mixtures of HS(CH$_2$)$_{11}$OH and HS(CH$_2$)$_{11}$CH$_3$. On all three, the wettability of the interfaces covers the range between the extremes: $\theta_a^{H_2O}$ = ~10° and ~115°. Values of the advancing contact angle of water can be related to their composition by Cassie's expression. The similarity in wettabilities of these surfaces and the fact that wettability is related to surface composition by a simple linear relationship both argue that CH$_2$OH and CH$_2$CH$_3$ functional groups behave approximately independently at the monolayer–air (water) interface.

Introduction

Long-chain alkanethiols (HS(CH$_2$)$_n$CH$_3$) adsorb from solution onto the surfaces of copper, silver, and gold and form densely packed, oriented monolayer films (self-assembled monolayers, SAMs) that are attached to the surface as metal thiolates (RS⁻M⁺).[3-23] On gold, alkanethiolate monolayers, derived from

alkanethiols or alkyl disulfides, have provided systems used for studies of wetting,[7-13] adhesion,[14] protein adsorption,[15,16] and electrochemistry.[16-20] These assemblies offer a high degree of control over the thickness of the monolayer and accommodate a

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(2) Shell Foundation Pre-doctoral Fellow 1987–1988.

(3) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991,** *113,* 7152–7167.

(4) Walczak, M. W.; Chung, C.; Stole, S. M.; Widrig, C. A.; Porter, M. D. *J. Am. Chem. Soc.* **1991,** *113,* 2370–2378.

(5) (a) Raman spectroscopy: Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991,** *113,* 3629–3637. (b) X-ray and helium diffraction: Fenter, P.; Eisenberger, P.; Li, J.; Camillone, N., III; Bernasek, S.; Scoles, G.; Ramanarayanan, T. A.; Liang, K. S. *Langmuir* **1991,** *7,* 2013–2016. (c) Sum-frequency vibrational spectroscopy: Bain, C. D.; Davies, P. B.; Ong, T. H.; Ward, R. N.; Brown, M. A. *Langmuir* **1991,** *7,* 1563–1566.

(6) (a) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983,** *105,* 4481–4483. (b) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987,** *109,* 2358–2368.

(7) 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.

(8) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988,** *110,* 5897–5898.

(9) (a) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988,** *110,* 3665–3666. (b) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988,** *110,* 6560–6561. (c) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989,** *111,* 7164–7175.

(10) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989,** *111,* 7155–7164.

(11) Bain, C. D.; Whitesides, G. M. *Langmuir* **1989,** *5,* 1370–1378.

(12) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1990,** *112,* 570–579.

(13) For reviews, see: (a) Bain, C. D.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 506–516. (b) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990,** *6,* 87–96.

(14) (a) Allara, D. L.; Heburd, A. F.; Padden, F. J.; Nuzzo, R. G.; Falcon, D. R. *J. Vac. Sci. Technol., A* **1983,** *1,* 376–382. (b) Stewart, K. R.; Whitesides, G. M.; Godfried, H. P.; Silvera, I. F. *Rev. Sci. Instrum.* **1986,** *57,* 1381–1383. (c) Ulman, A.; Tillman, N. *Langmuir* **1989,** *5,* 1418–1420. (d) Czanderna, A. W.; King, D. E.; Spaulding, D. *J. Vac. Sci. Technol., A* **1991,** *9,* 2607–2613.

(15) (a) Pale-Grosdemange, C.; Simon, E. S.; Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991,** *113,* 12–20. (b) Häussling, L.; Michel, B.; Ringsdorf, H.; Rohrer, H. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 569–572. (c) Prime, K. L.; Whitesides, G. M. *Science (Washington, D.C.)* **1991,** *252,* 1164–1167. (d) Häussling, L.; Ringsdorf, H.; Schmitt, F.-J.; Knoll, W. *Langmuir* **1991,** *7,* 1837–1840.

(16) (a) Allen, P. M.; Hill, H. A. O.; Walter, N. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1984,** *178,* 69–86. (b) Armstrong, F. A.; Hill, H. A. O.; Walton, N. J. *Acc. Chem. Res.* **1988,** *21,* 407–413. (c) Tarlov, M. J.; Bowden, E. F. *J. Am. Chem. Soc.* **1991,** *113,* 1847–1849.

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

(18) Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* **1990,** *6,* 682–691.

(19) Nonelectroactive n-alkanethiols: (a) Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984,** *106,* 6107–6108. (b) Sabatini, E.; Rubinstein, I.; Maoz, R.; Sagiv, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1987,** *219,* 365–371. (c) Sabatini, E.; Rubinstein, I. *J. Phys. Chem.* **1987,** *91,* 6663–6669. (d) Finklea, H. O.; Avery, S.; Lynch, M.; Furtsch, T. *Langmuir* **1987,** *3,* 409–413. (e) Bunding Lee, K. A.; Mowry, R.; McLennan, G.; Finklea, H. O. *J. Electroanal. Chem. Interfacial Electrochem.* **1988,** *246,* 217–224. (f) Rubinstein, I.; Steinberg, S.; Tor, Y.; Shanzer, A.; Sagiv, J. *Nature* **1988,** *332,* 426–429. (g) Creager, S. E.; Collard, D. M.; Fox, M. A. *Langmuir* **1990,** *6,* 1617–1620. (h) Miller, C.; Cuendet, P.; Grätzel, M. *J. Phys. Chem.* **1991,** *95,* 877–886. (i) Miller, C.; Grätzel, M. *J. Phys. Chem.* **1991,** *95,* 5225–5233.

(20) Electroactive n-alkanethiols: (a) Bunding Lee, K. A. *Langmuir* **1990,** *6,* 709–712. (b) Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujsce, A. M. *J. Am. Chem. Soc.* **1990,** *112,* 4301–4306. (c) Obeng, Y. S.; Bard, A. J. *Langmuir* **1991,** *7,* 195–201. (d) Hickman, J. J.; Ofer, D.; Zou, C.; Wrighton, M. S.; Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991,** *113,* 1128–1132. (e) Chidsey, C. E. D. *Science (Washington, D.C.)* **1991,** *251,* 919–922. (f) Hickman, J. J.; Ofer, D.; Laibinis, P. E.; Whitesides, G. M.; Wrighton, M. S. *Science (Washington, D.C.)* **1991,** *252,* 688–691. (g) Collard, D. M.; Fox, M. A. *Langmuir* **1991,** *7,* 1192–1197. (h) Uosaki, K.; Sato, Y.; Kita, H. *Langmuir* **1991,** *7,* 1510–1514. (i) Hickman, J. J.; Laibinis, P. E.; Auerbach, D. I.; Zou, C.; Gardner, T. J.; Whitesides, G. M.; Wrighton, M. S. *Langmuir*, in press.

(21) (a) Diem, T.; Czajka, B.; Weber, B.; Regen, S. L. *J. Am. Chem. Soc.* **1986,** *108,* 6094–6095. (b) Fabianowski, W.; Coyle, L. C.; Weber, B. A.; Granata, R. D.; Castner, D. G.; Sadownik, A.; Regen, S. L. *Langmuir* **1989,** *5,* 35–41.

(22) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990,** *112,* 558–569.

(23) (a) Sum-frequency vibrational spectroscopy: Harris, A. L.; Chidsey, C. E. D.; Levinos, N. J.; Loiacono, D. N. *Chem. Phys. Lett.* **1987,** *141,* 350–356. See also ref 5c. (b) TEM: Strong, L.; Whitesides, G. M. *Langmuir* **1988,** *4,* 546–558. See ref 18 for a reanalysis of part of the data in this paper. (c) Helium diffraction: Chidsey, C. E. D.; Liu, G.-Y.; Rowntree, P.; Scoles, G. *J. Chem. Phys.* **1989,** *91,* 4421–4423. Camillone, N., III; Chidsey, C. E. D.; Liu, G.-Y.; Putvinski, T. M.; Scoles, G. *J. Chem. Phys.* **1991,** *94,* 8493–8502. (d) IR spectroscopy: Nuzzo, R. G.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* **1990,** *93,* 767–773. See also refs 3, 17, and 22. (e) STM: Widrig, C. A.; Alves, C. A.; Porter, M. D. *J. Am. Chem. Soc.* **1991,** *113,* 2805–2810. (f) X-ray diffraction: Samant, M. G.; Brown, C. A.; Gordon, J. G., III *Langmuir* **1991,** *7,* 437–439. See ref 5b for a reexamination of part of the data in this paper. (g) Raman spectroscopy: Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991,** *113,* 8284–8293.

wide range of polar and nonpolar tail groups at the opposite terminus of the polymethylene chain from the thiol group (and thus at the interface between the SAM and the vapor or liquid phase contacting it). To date, the self-assembling system reported to be capable of generating the widest variety of organic interfaces is that based on adsorption of ω-substituted alkanethiols on gold.[7-15,18,20-22] Here we report that the chemistry described for alkanethiolates on gold can be readily extended to alkanethiolates on silver and, with greater experimental difficulty, on copper. We also provide data that suggests that, while the alkanethiolate monolayers on silver and copper have structures that are distinct from (although closely related to) those formed on gold, similar wettabilities are observed for corresponding SAMs on all three metals. We and others have described extensive structural studies of *unsubstituted* alkanethiolates on gold,[23] silver,[3-5] and copper.[3] The emphasis in the present paper is on alkanethiolates bearing terminal substituents, especially polar ones. Ulman et al.[24] have reported that monolayers formed by adsorption of $HS(CH_2)_{11}OH$ on silver and gold have different wettabilities: $\theta_a^{H_2O} \sim 20°$ and $<10°$, respectively. We find the wettability of SAMs on silver and gold derived from hydroxyl-terminated alkanethiols, including those derived from $HS(CH_2)_{11}OH$, to be the same, although we have observed higher values of $\theta_a^{H_2O}$ on silver whose surface has oxidized.

Many self-assembling systems now exist that can generate low-energy surfaces;[3-7,25,26] however, the number capable of generating high-energy surfaces, *in one assembly step*, are few. For example, while *n*-alkanoic acids adsorb onto various metal oxides and form oriented, oleophobic monolayers,[26] ω-hydroxy- and ω-aminoalkanoic acids adsorb and form poorly organized films that are not wet by water (probably because they form "looped" structures with polar functionalities in both α- and ω-positions coordinated to the surface). Relatively hydrophilic surfaces ($\theta_a^{H_2O} \approx 30-50°$) have been prepared on silica in a two-step procedure: first, adsorption of an alkyltrichlorosilane having a terminal olefin, ester, or alkyl sulfide group on silica;[27-29] second, chemical transformation of the nonpolar terminal group into a more polar group (carboxylic acid,[27] alcohol,[27,28] or sulfone[29]). This type of system has two disadvantages. First, the monolayers of alkyl-siloxanes on silica are probably intrinsically less ordered than SAMs on gold and silver[30] and are unquestionably more difficult to prepare in highly-ordered form; second, the reactions used to convert functionalities present in these SAMs to more polar forms certainly proceed in yields less than 100%.[31] Thus, the alkyl-siloxane monolayers having polar terminal functionality are probably disordered both in structure and in composition at their termini.

In contrast, interfaces that are both polar and highly wettable (alcohols,[7,18,22] carboxylic acids,[7,11,18,22] phosphocholines,[21] and amides[22]) have been prepared by adsorption of the corresponding

alkanethiols onto gold surfaces. We believed the ability of gold to discriminate between hard and soft[32] tail groups could be extended to surfaces of copper and silver.[33]

In a previous paper,[3] we have shown that *n*-alkanethiols adsorb onto copper and silver and form oriented, densely packed monolayers. These SAMs differ in one respect from those formed on gold; X-ray photoelectron spectroscopy (XPS) and IR spectroscopy indicated that the alkyl chains are oriented closer to the perpendicular to the surface of the metal on copper and silver than on gold (cant angles relative to the surface normal are 13° (copper and silver) and 28° (gold)). We note that the SAMs studied in that report[3] and here exhibited no (or little) surface oxide on silver and gold; the monolayers formed on copper were supported on an interphase that contained oxide even though exposure of the unfunctionalized surface to the atmosphere was minimized.

Results and Discussion

Films of copper, silver, and gold were prepared by evaporation of the metals onto precut slides of Cr-primed Si(100) using an electron beam. All three metal surfaces are microscopically rough. Scanning tunneling microscopy (STM) and scanning electron microscopy (SEM) examinations of representative gold surfaces suggest a surface comprising irregular "mounds" approximately 100 Å across and 20–30 Å high.[34] Surfaces of copper and silver appear by SEM similar to those formed of gold;[3] we have not characterized the surfaces of copper and silver by STM but suspect that the copper surface is rougher than the other two metal surfaces.

The slides were immersed in 1 mM deoxygenated ethanolic solutions[35] of various ω-terminated alkanethiols for 2–12 h and characterized by measurement of contact angle and XPS. Some SAMs on copper (X = CH_3, $CH=CH_2$) were prepared from isooctane and exhibited lower hysteresis than corresponding SAMs formed from ethanol. The evaporated films of copper and silver were transferred to solution under a flow of argon; films of gold were transferred under air. Table I summarizes the advancing and receding contact angles of water and hexadecane on the resulting SAMs.

In general, the wetting behaviors observed on the monolayers prepared on silver and copper are similar to those prepared on gold; the hysteresis in the contact angles of water is generally greater on the copper surfaces. We believe that this increase is probably due to the roughening of the copper (oxide)–air (or monolayer) interface that occurs during oxidation and subsequent adsorption of the thiol. We note that the range of wettabilities, for $\theta_a^{H_2O} \approx 120°$ to $\theta_a^{H_2O} < 15°$, demonstrated on copper, silver, and gold cannot be achieved presently in other self-assembling systems.

The only organic groups that yielded highly hydrophilic surfaces ($\theta_a^{H_2O} < 20°$) are those that exposed groups capable of hydrogen-bond donation (OH, CO_2H, $CONH_2$). Alkanethiols terminating in X = OH or CO_2H did not always yield SAMs on copper that were as hydrophilic as those formed on gold or silver; for X = OH, SAMs were not wet by water only for long-chain (*n* > 16) adsorbates. Carboxylic acids and alcohols will form monolayers on most (if not all) metal oxides;[26] we believe that the films formed on our slightly oxidized copper surfaces probably consist, in part, of "looped"[36] and/or "inverted" structures. These

(24) Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir* **1989**, *5*, 101–111.

(25) (a) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, *1*, 513–538. (b) Shafrin, E. G.; Zisman, W. A. *J. Colloid Sci.* **1952**, *7*, 166–177. (c) Blackman, L. C. F.; Dewar, M. J. S.; Hampson, H. *J. Appl. Chem.* **1957**, *7*, 160–171. (d) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92–98. (e) Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465–496. (f) Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365–385.

(26) (a) Schulman, F.; Zisman, W. A. *J. Colloid Sci.* **1952**, *7*, 465–481. (b) Bigelow, W. C.; Brockway, L. O. *J. Colloid Sci.* **1956**, *11*, 60–68. (c) Allara, D. L.; Nuzzo, R. G. *Langmuir* **1985**, *1*, 45–52. (d) Schlotter, N. E.; Porter, M. D.; Bright, T. B.; Allara, D. L. *Chem. Phys. Lett.* **1986**, *132*, 93–98.

(27) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074–1087.

(28) (a) Netzer, L.; Sagiv, J. *J. Am. Chem. Soc.* **1983**, *105*, 674–676. (b) Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *99*, 235–241. (c) Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *100*, 67–76. (d) Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir* **1989**, *5*, 101–111.

(29) Tillman, N.; Ulman, A.; Elman, J. F. *Langmuir* **1989**, *5*, 1020–1026.

(30) Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *110*, 6136–6144.

(31) The wettabilities of the alcohol and carboxylic acid surfaces generated by chemical transformation of less polar terminal groups on alkylsiloxane monolayers ($\theta_a^{H_2O} \approx 30-55°$)[27,28] are significantly less than that found on surfaces formed on gold from the corresponding ω-terminated alkanethiols or disulfides ($\theta_a^{H_2O} < 15°$).[7,11,22]

(32) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539. (b) Huheey, J. E. *Inorganic Chemistry*; Harper & Row: New York, 1978; pp 276–280.

(33) For an example of the degree of discrimination possible between hard (CO_2H) and soft (SH) adsorbates for hard (Al_2O_3) and soft (Au) surfaces, see: Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. *Science (Washington, D.C)* **1989**, *245*, 845–847.

(34) Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.*, submitted for publication.

(35) Ethanol was chosen as the contacting solvent due to its low cost and toxicity and its previous use to generate alkanethiolate surfaces on gold of a wide range of wettabilities.[6-11,22] Less polar solvents yield ω-hydroxyalkanethiolate monolayers on gold of decreased hydrophilicity.[10]

(36) Allara, D. L.; Atre, S. V.; Ellinger, C. A.; Snyder, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1852–1854.

Table I. Static Advancing and Receding Contact Angles of Water and Hexadecane (HD) on Films Prepared by Adsorption of $HS(CH_2)_nX$ on Surfaces of Gold, Silver, and Copper

compd no.	n	X	molecular length[b]	contact angles (advancing, receding; deg)[a]					
				Au		Ag		Cu	
				H_2O	HD	H_2O	HD	H_2O	HD
1	2	$(CF_2)_5CF_3$	10	119, 106	71, 62	121, 110	79, 60	122, 106	81, 59
2	11	$OCH_2CF_2CF_3$	17	118, 105	71, 62	119, 111	75, 61	119, 99	69, 44
3	7	CH_3[c]	10	112, 103	46, 35	107, 93	45, 33	115, 98	44, 31
4	11	CH_3[c]	14	115, 104	49, 36	113, 99	46, 35	120, 99	46, 28
5	17	CH_3[c]	20	115, 105	48, 36	116, 103	49, 35	120, 103	48, 32
6	21	CH_3[c]	24	117, 100	49, 38	115, 103	49, 36	117, 102	45, 34
7	17	$CH=CH_2$[c]	21	105, 100	38, 28	108, 100	44, 34	117, 96	31, 24
8	11	$OCOCF_3$[d]	16	93, 83	60, 28	93, 77	64, 32	100, 85	58, 30
9	10	$CO_2CH_2CH_3$	16	89, 77	45, 28	89, 71	38, 19	93, 69	31, –
10	11	Cl	13	89, 77	<10, –	89, 77	<10, –	95, 80	<10, –
11	11	OCH_3	15	85, 72	37, 11	84, 66	38, 20	87, 57	32, –
12	11	CN	14	68, 61	<10, –	74, 65	<10, –	72, 52	<10, –
13	16	CN	19	70, 62	<10, –	75, 63	<10, –	77, 49	<10, –
14	21	CN	24	74, 62	<10, –	78, 60	<10, –	80, 60	<10, –
15	11	$CONHCH_3$	16	76, 64	31, –	82, 65	29, –	e	e
16	10	CO_2CH_3	15	74, 61	38, 25	72, 64	35, 22	70, 49	22, –
17	10	OH	13	<15, –	<10, –	<15, –	<10, –	<15, –	<10, –
18	11	OH	14	<15, –	<10, –	<15, –	<10, –	<15, –	<10, –
19	19	OH	22	<15, –	<10, –	<15, –	<10, –	26, –	<10, –
20	22	OH^f	25	25, –	<10, –	21, –	<10, –	44, 20	<10, –
21	10	$CONH_2$	14	<15, –	<10, –	<15, –	<10, –	<15, –	<10, –
22	15	$CONH_2$	19	<15, –	<10, –	<15, –	<10, –	17, –	<10, –
23	10	CO_2H	14	<15, –	<10, –	<15, –	<10, –	35–50, –	<10, –
24	15	CO_2H	19	<15, –	<10, –	<15, –	<10, –	53, 25	<10, –
25	21	CO_2H	25	<15, –	<10, –	<15, –	<10, –	50, 25	<10, –

^{a} HD = hexadecane. A dash indicates a receding contact angle for a contacting liquid that could not be removed from the surface. For these systems, $\theta_r \cong 0°$. The reproducibility in the value of θ is $\sim\pm3°$. ^{b} Molecular length is defined as the number of contiguous atoms in the adsorbed molecule comprising the monolayer metal/$S(CH_2)_nX$. These values are used in Figure 1. ^{c} The SAM on copper was formed from isooctane. SAMs prepared on copper from this thiol from ethanol routinely exhibited greater hystereses (cos θ_r – cos θ_a) than SAMs adsorbed from isooctane. ^{d} Prepared by reaction of **18** with 5% trifluoroacetic anhydride/hexanes for 30 s. ^{e} SAMs on copper were difficult to obtain in high quality. The wetting properties of our best samples were as follows: $\theta_a{}^{H_2O} = 65$–$75°$, $\theta_r{}^{H_2O} = 36°$, $\theta_a{}^{HD} = 17°$, $\theta_r{}^{HD} \cong 0°$. ^{f} The value $\theta_a{}^{H_2O} \approx 20°$ has been reported for SAMs on gold derived from $HS(CH_2)_{21}OH$ (Evans, S. D.; Sharma, R.; Ulman, A. *Langmuir* **1991**, 7, 156–161).

overall structures would expose a hydrophobic, disordered interface to the contacting liquid (vide infra). Alkanethiols terminating in polar groups adsorbed on silver surfaces that contained an oxide interphase also yielded less hydrophilic surfaces; the contact angles reported here on silver (Table I, **17–25**) were only obtained when exposure of the evaporated silver to atmosphere was minimized. The adsorption of some fraction of the tail groups to the oxide surface may explain some of the higher contact angles of water observed by Ulman and co-workers for polar organic surfaces formed on silver.[24] We note that we have been able to reproduce the higher contact angles of water reported by Ulman et al. by allowing the silver to oxidize sufficiently before exposure to an ω-hydroxyalkanethiol.

The highly hydrophilic surfaces (X = OH, $CONH_2$, and CO_2H; **17–21**) provide an example of the sensitivity of wetting of these systems to structure. Replacement of a hydrogen atom in these structures by a methyl group (X = OCH_3, $CONHCH_3$, and CO_2CH_3; **11**, **15**, and **16**) is sufficient to change these very hydrophilic surfaces to hydrophobic surfaces ($\theta_a{}^{H_2O} \approx 70$–$90°$) that are also no longer wet by hexadecane; similar effects have been observed previously.[8,22,37]

The monolayers formed on the three metal surfaces were characterized by XPS to determine their structural similarity to films formed from simple n-alkanethiols (Figure 1); XPS can be used as a measure of the thickness of a film by determining the attenuation of photoelectrons from the underlying substrate by the adsorbed layer.[38] We have shown previously for n-alkanethiolate monolayers formed on the three metals that conclusions concerning the structure of the SAM drawn from XPS attenuations agreed with those from IR.[3,39] For this study, the variations

in head groups complicate comparison; we adopt the convention of comparing the intensities of photoelectrons due to the substrate to the number of atoms that extend from the sulfur to the end of the tail group in the adsorbed molecule (see Table I). While this treatment is qualitative and does not take full account of differences in the structures of the various tail groups, it provides a useful comparison. The degree of attenuation is also a function of the kinetic energy (KE) of the photoelectrons,[40] and we compare peaks of similar energies, that is, in Figure 1, Au(4d) (KE ≈ 1143 eV) with Ag(3d$_{5/2}$) (KE = 1119 eV); Au(4f$_{7/2}$) (KE = 1402 eV) with Cu(3p) (KE ≈ 1410 eV). Each datum was obtained in ~3 min, and the damage to the monolayers in this interval due to exposure to X-rays was negligible.[41] Figure 1 shows that the attenuation and, thus, the relative thicknesses of the monolayers containing tail groups of differing polarity but commensurate in

(37) Wilson, M. D.; Ferguson, G. S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 1244–1245.

(38) The intensity of the photoelectron peak due to an underlayer decreases exponentially with the thickness of the overlayer due to inelastic scattering of photoelectrons from the underlayer with the overlayer (Briggs, D.; Seah, M. *Practical Surface Analysis*; Wiley: Chichester, 1983; p 211).
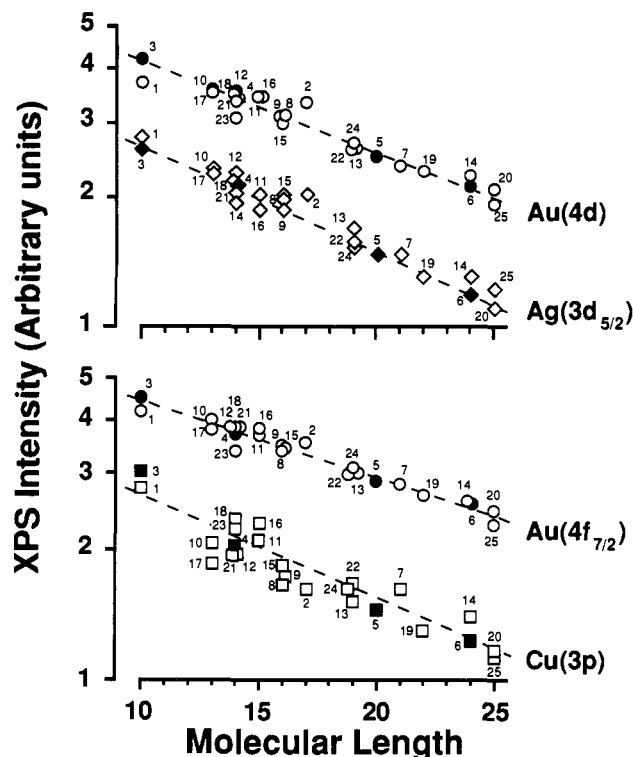
(39) IR spectroscopy could also be used to characterize the structure of these monolayers although absolute determinations of structure by IR spectroscopy is confounded by choice of a reference state. We believe that once a standard (n-alkanethiols) has been evaluated,[3,4,17,22] comparison to it by XPS is not only more convenient but probably also no less accurate or precise. The thickness of the SAM can be estimated from the attenuation of photoelectrons by the film.[38] Assuming the SAM to contain trans-extended polymethylene chains, the thickness is related to the angle at which the adsorbate is oriented on the metal. Details pertaining to orientation of tail groups and twisting of the polymethylene chains are, however, determinable by IR spectroscopy and not by XPS.

(40) Seah, M. P.; Dench, W. A. *Surf. Interface Anal.* **1979**, *1*, 2–11.

(41) Characterization of organic SAMs by XPS has been reported to damage the SAM.[22] The rate of damage is, however, a function of spectrometer design, particularly whether the incident X-rays are monochromatized. Using our instrument, we observed small changes in the intensities of peaks due to the underlying substrates or tail groups after 1 h of exposure to monochromatized Al Kα X-rays (both ≤10%). The wetting properties of the SAM do, however, change with exposure to the X-rays, presumably due to loss of the tail group and revelation of underlying hydrocarbon. We therefore obtained the wetting data given in Table I and Figures 2 and 3 on SAMs prior to their characterization by XPS. For examples of X-ray induced damage to SAMs, see the following: Bain, C. D., Ph.D. Thesis, Harvard University, 1988. Laibinis, P. E.; Graham, R. L.; Biebuyck, H. A.; Whitesides, G. M. *Science (Washington, D.C.)* **1991**, *254*, 981–983.

Figure 1. Intensity of photoelectrons due to the underlying metal substrate for various monolayers adsorbed on the surfaces of copper ($\square$), silver ($\lozenge$), and gold ($\bigcirc$) from absolute ethanol. We define "molecular length" as the number of contiguous atoms in the adsorbate spanning the monolayer. (For example, for metal/$SCH_2CO_2CH_3$ the molecular length would be 6.) The numeric labels refer to compounds listed in Table I. Absolute photoelectron intensities are a function of instrumental parameters, and the sets of data have been offset vertically to facilitate comparison; only the slopes are important here. The kinetic energies of photoelectrons for each graph are similar: $Au(4f_{7/2}) = 1402$ eV and $Cu(3p) = 1412$ eV; $Au(4d) = 1143$ eV and $Ag(3d_{5/2}) = 1119$ eV. The filled symbols correspond to SAMs derived from n-alkanethiols (X = CH_3). Dashed lines were determined from linear least-squares fits to data obtained from adsorption of n-alkanethiols on the three metals; the higher slopes obtained on copper and silver demonstrate that the SAMs formed on these metals are oriented closer to the surface normal than those formed on gold: $Au(4d) = -0.049$ vs $Ag(3d_{5/2}) = -0.057$; $Au(4f_{7/2}) = -0.041$ vs $Cu(3p) = -0.051$.

size with the polymethylene chains are similar to those derived from n-alkanethiols throughout a series on a particular metal. We stress that the XPS data presented here imply that *the functional groups are supported on a hydrocarbon layer* (($CH_2)_n$) *that is analogous in thickness and thus in packing density to simple n-alkanethiolate monolayers on the various metals.*[42] These differences in the change in thickness with atomic length between SAMs formed on the three metals suggest that the orientation of the axis of the polymethylene chain is closer to the normal to the surface on copper and silver than on gold. The XPS data do not, however, indicate anything about fine details of structure, especially the orientation of the tail groups or the order at the monolayer–air interface. At room temperature, calculations by Klein et al.[43] indicate the tail groups to be dynamic and disordered.[44]

The XPS attenuation of the films formed on copper by exposure to $HS(CH_2)_nCO_2H$ or $HS(CH_2)_{19,22}OH$ suggests that the packing density of the film approximates a densely packed, oriented monolayer. The wettabilities of these films are, however, inconsistent with the formation of an interface comprising densely packed carboxylic acid or hydroxyl groups (vide supra). The films were examined further by XPS. High-resolution spectra of the

(42) Nuzzo et al.[22] have shown by IR spectroscopy that ω-substituted-pentadecanethiolate monolayers on gold have similar structures when the head group is commensurate in size with the polymethylene chain.
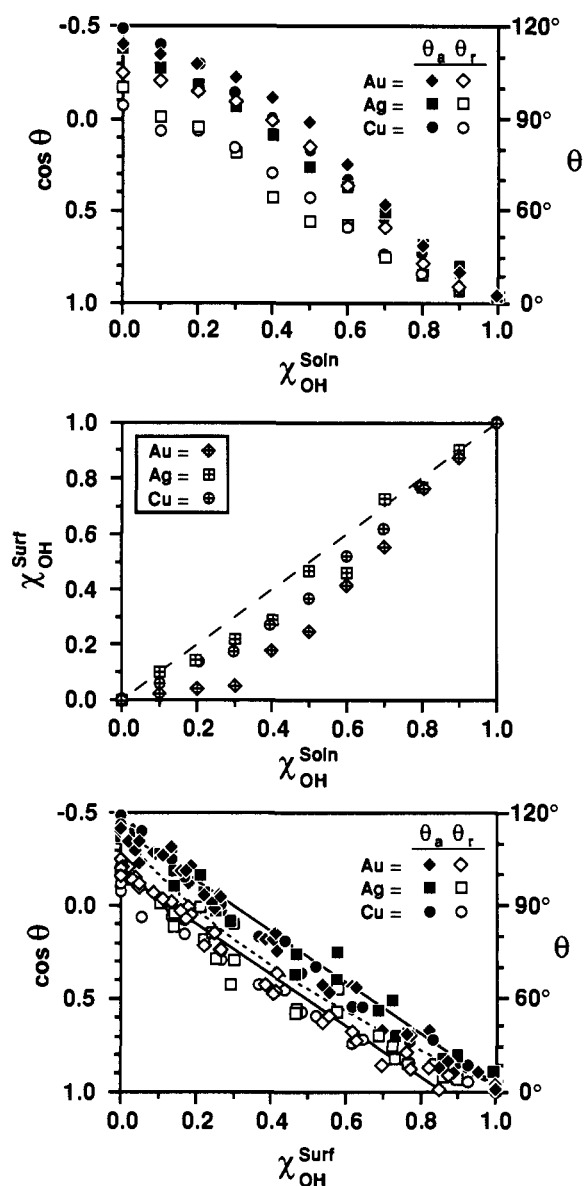
Figure 2. Comparison of monolayers adsorbed on copper (O), silver ($\square$), and gold ($\lozenge$) from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$ dissolved in ethanol after 2-h exposure. Solutions were 1 mM in total thiol concentration. Advancing and receding contact angles (filled and open symbols, respectively) were measured on static drops of water; errors are estimated to be ±3°. Surface compositions (patterned symbols) were determined from XPS by scaling the O(1s) signal to that obtained on the pure $HS(CH_2)_{11}OH$-derived monolayer; the background level of oxygen on copper (determined from the pure $HS(CH_2)_{11}CH_3$-derived monolayer) was subtracted from all copper samples prior to analysis.[46] We estimate the error in χ^{surf} to be ±0.05. Cassie's equation[47] (solid lines; bottom graph) relates the surface composition linearly to the wettability of the monolayer by water. Israelachvili and Gee's equation[48] (dashed line) does not describe the relation between advancing contact angle and surface composition as well as Cassie's equation. The lowest panel includes data obtained from samples that were exposed to the contacting solutions for 2–48 h.

$S(2p)$ region revealed a broad envelope that could not be fit by a single spin–orbital doublet. The presence of intensity at binding energies that are slightly higher ($\Delta = 1$ eV) than those expected for metal thiolates suggests that some of the sulfur-containing species are present as thiols. Similar wetting and XPS features could be observed on silver that had been highly oxidized.

Mixed Monolayers Adsorbed from Ethanol Solution. In a further comparison of the characteristics of SAMs on the three metals, we determined contact angles on mixed monolayers[9,10] prepared by adsorbing $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{11}OH$ from 1 mM ethanolic solutions containing mixtures of these two com-

pounds.[45] The metals were exposed to the contacting solution for 2 h. The wettabilities of the resulting monolayers for various compositions of the solutions and of the resulting SAMs are plotted in Figure 2. The surface compositions were determined from XPS by comparing the intensity of the O(1s) peak in the mixed monolayer to the intensity of the monolayer derived from pure HS(CH₂)₁₁OH. Determinations of the surface compositions on copper were complicated by the presence of surface oxide and are therefore slightly less accurate than on gold and silver.[46] The three systems were dynamic: the films incorporated more do-decanethiol and became increasingly hydrophobic with extended exposure to the ethanolic solutions. The relation between wettability and surface composition did not change with the length of time the slides were exposed to the contacting solutions, and we have included data from longer exposure times in the lower panel of Figure 2.

On all three metals, the SAMs exhibited similar wettabilities at the same value of the mole fraction of the hydroxyl-containing component in solution (χ_{OH}^{soln}) or on the surface (χ_{OH}^{surf}). The two alkanethiols adsorb on the three metals, forming monolayers of similar compositions, and the wettability of these mixed monolayers is better described by Cassie's equation[47] (eq 1) than by eq 2 suggested by Israelachvili and Gee[48] (Figure 2). In eqs 1

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{1}$$

$$(1 + \cos\theta)^2 = f_1(1 + \cos\theta_1)^2 + f_2(1 + \cos\theta_2)^2 \tag{2}$$

and 2, f_n is defined as the fractional area of the surface that is type n, and θ_n is defined as the contact angle on a pure homogeneous surface of type n; hydroxyl and methyl groups are sufficiently similar in size that we assume f_n and χ_n^{surf} are equivalent for the system studied here. We discuss the comparison of these equations further below.

The similarity in surface compositions (χ_{OH}^{surf}) at a common value of solution composition (χ_{OH}^{soln}) is remarkable, given the differences in the structures of the monolayers, the strength of the various thiolate–metal bonds, and most importantly, the different chemistries that must be occurring during adsorption of the thiols onto surfaces having differing amounts of oxide. This similarity is particularly striking for silver (which has an oxide surface before exposure to thiol) and gold (which does not). It is probable that the interfaces between the SAM and the contacting liquid on different metals have significantly different structures at the atomic scale for a number of reasons: the microscopic topology and lattice structure of the underlying metals are undoubtedly different; the cant angle and packing density of the chains, and the extent of order of the tailgroup region, in the SAMs are probably different; the extent of phase segregation of the two components of the mixed SAMs may be different. Despite these differences, the wettabilities are similar. We conclude that wettability must be sensitive to the composition of the interface between the SAM and the liquid (especially the mole fraction of the different tail groups present) but less sensitive to at least some aspects of the ordering of these groups at the interface.

The hysteresis in the contact angles of water appears constant over all surface compositions (and wettabilities) on each of the three metals. This observation suggests that any islanded domains that may have formed have similar sizes on a given metal. The
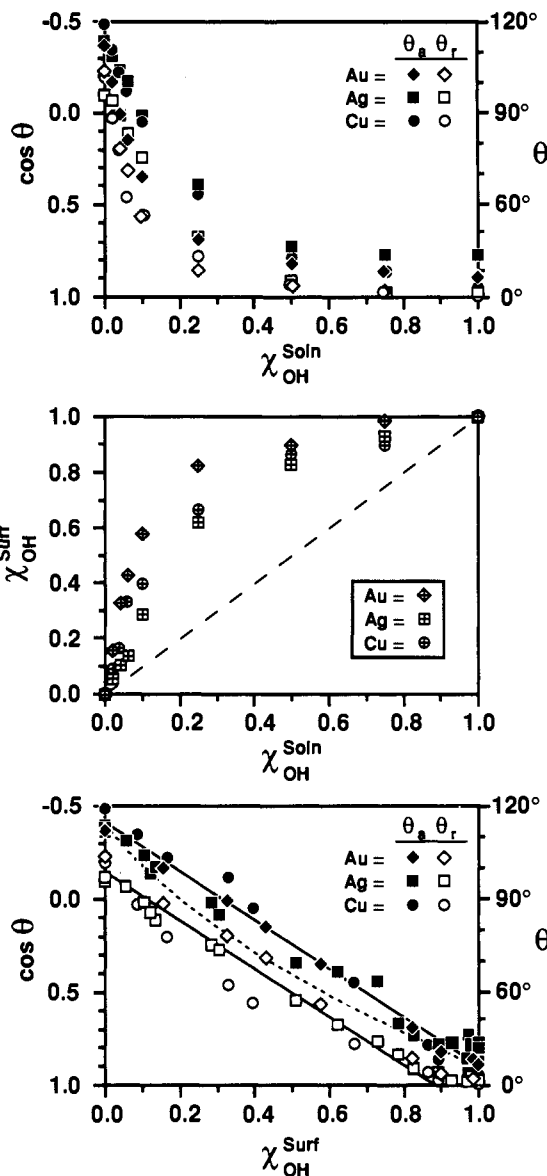

Figure 3. Comparison of monolayers adsorbed on copper (O), silver (□), and gold (◊) from mixtures of HS(CH₂)₁₁OH and HS(CH₂)₁₁CH₃ dissolved in isooctane after 1-h exposure. Solutions were 1 mM in total thiol concentration. Data were analyzed and are presented as in Figure 2.

hysteresis on each of the metals is, however, significantly different (Cu > Ag > Au). Because the surface roughness of the metals may be different, hysteresis cannot be related directly to differences in the structures of the monolayers.

Mixed Monolayers Adsorbed from Isooctane Solution. We also examined whether the characteristics of the mixed monolayers on the three metals differed in their response to the solvent used in their preparation. Figure 3 gives data, using isooctane as a solvent, that parallel those in Figure 2 using ethanol. Bain et al. have shown that the preference of alkanethiols terminated with polar functional groups for a gold surface could be dramatically increased relative to nonpolar alkanethiols by using a less polar solvent in adsorption of the SAM.[10] Figure 3 shows that similar behaviors occur on all three metals using isooctane as the solvent for the alkanethiols, and that all three differ in similar ways from monolayers formed from ethanol. While the CH₃- and CH₂OH-terminated thiols competed about equally for the metal surfaces from ethanol, the latter absorbs preferentially from isooctane. With continued exposure to the contacting solution, χ_{OH}^{surf} increases and the film becomes more hydrophilic. Although the adsorption profiles from isooctane are different from those performed from ethanol, the wetting data are again better de-

(43) (a) Hautman, J.; Klein, M. L. *J. Chem. Phys.* **1989**, *91*, 4994–5001. (b) Hautman, J.; Bareman, J. P.; Mar, W.; Klein, M. T. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2031–2037.

(44) At room temperature, it is difficult to imagine that the tail groups would adopt a single orientation. The structure of alkanethiolate monolayers on gold (by helium diffraction and IR, respectively) is more crystalline at low temperatures (~100 K) than at room temperature.[23c,d]

(45) For molecular-dynamics calculations of the wetting properties of pure SAMs on gold derived from CH₃(CH₂)₁₁SH and HO(CH₂)₁₁SH by H₂O, see: Hautman, J.; Klein, M. L. *Phys. Rev. Lett.* **1991**, *67*, 1763–1766.

(46) The different O(1s) peaks overlapped slightly (binding energy, peak width: oxide, 530.4 eV, ~2.0 eV; hydroxyl 533.0 eV, ~2.0 eV) but could be resolved via χ^2 analysis of the composite signal.

(47) Cassie, A. B. D. *Discuss. Faraday Soc.* **1948**, *3*, 11–16.

(48) Israelachvili, J. N.; Gee, M. L. *Langmuir* **1989**, *5*, 288–289.

scribed by eq 1 than eq 2 even though the hydrophilicity of the pure hydroxyl surface (χ_{OH}^{surf} = 1.0) is substantially less from isooctane on all three metals than from ethanol. Adsorption of hydroxyl-terminated thiols onto gold from a non-hydrogen-bonding solvent has been shown to result in SAMs that are less hydrophilic than those formed in ethanol.[10] We do not know the cause of this difference; two possibilities are (1) formation of hydrogen-bonded networks having different structures and (2) contamination of the polar interface by impurities in solvent.

Ulman et al.[49] have recently reported the presence of a wetting transition for hexadecane, bicyclohexyl, and methoxyethanol on SAMs on gold derived for mixtures of $CH_3(CH_2)_{11}SH$ and HO-$(CH_2)_{11}SH$. The data in Figures 2 and 3 clearly indicate that no wetting transition exists for water in these mixed monolayers on gold, silver, or copper. No significant departures from Cassie's equation were observed with SAMs adsorbed from ethanol or isooctane on any of the three metals studied here.

The Relation between Wettability and Surface Composition: Cassie vs Israelachvili–Gee. Both of these semiempirical equations are useful in correlating surface composition with wetting. In general, the two give similarly good correlations.[50] Israelachvili and Gee[48] have suggested eq 2 as an alternative to eq 1 "whenever the size of chemically heterogeneous patches approach molecular or atomic dimensions." The mixed SAMs should fit this description, provided they are not phase-separated into large islands. Here, it appears that SAMs prepared from mixtures of CH_3-$(CH_2)_{11}SH$ and $HO(CH_2)_{11}SH$ are better described by eq 1 than eq 2. In contrast, Bain et al. have shown that mixed SAMs on gold prepared from $CH_3(CH_2)_{10}SH$ and $HO(CH_2)_{11}SH$ are more hydrophilic than Cassie's relation would suggest.[10] We have reanalyzed their data and find that the wettability of the mixed monolayers is described well by eq 2.[51] Why the apparent disagreement in two very similar systems? One possible hypothesis, based on the respective assumptions inherent in eqs 1 and 2, might be that the former system forms SAMs that are highly islanded and the latter does not. Further studies on these and other systems will be required to determine the degree of phase separation that may be present in these systems and the factors that affect the magnitude of separation.

Conclusions

ω-Terminated alkanethiols form oriented monolayers on copper, silver, and gold surfaces that exhibit similar wetting properties, although they differ significantly in structure (specifically in the cant angles of the trans-extended chains: on gold, 28°; on copper and silver, 13°), and very probably in other details as well: roughness and morphology of the metal surfaces and extent of phase separation in mixed SAMs. These probable and established differences notwithstanding, we observed no significant differences in the wettability of hydroxyl-terminated monolayers on the three metals. The three metals accommodate a variety of tail groups; organic surfaces of a wide range of wettabilities ($\theta_a^{H_2O}$ of <15° to ∼115°) can be generated on each. Monolayers prepared on

each of these metals from mixtures of alkanethiols of similar chain lengths containing different tail groups show similar relations between the compositions of the monolayers and the compositions of the solutions from which they were formed[52] and exhibit similar wettabilities. The wettabilities of the mixed monolayers derived from alkanethiols having the same number of methylene groups are better described by the relation of Cassie[47] than of Israelachvili and Gee.[48] No wetting transition[49] was observed with water on SAMs on gold, silver, or copper prepared from mixtures of HS-$(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$.

Experimental Section

Supplementary Material Available: Details of the preparation of 11-(2,2,3,3,3-pentafluoropropoxy)undecanethiol, ethyl 11-mercaptoundecanoate, 11-cyano-1-undecanethiol, 16-cyano-1-hexadecanethiol, 21-cyano-1-heneicosanethiol, 10-mercapto-1-decanol, 22-mercapto-1-docosanol, and 11-mercaptoundecanamide (10 pages). Ordering information is given on any current masthead page.

(49) Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E.; Chang, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 1499–1506.

(50) Ulman et al. have recently used eqs 1 and 2 to describe the relation between the advancing contact angle of water and the composition of SAMs on gold derived from mixtures of $CH_3(CH_2)_{11}SH$ and $HO(CH_2)_{11}SH$ (the thiols used in our study) (Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E. *Adv. Colloid Interface Sci.*, in press). While they found that the data were described well by these equations, their data contained sufficient scatter that it was not possible to conclude which equation fit the data better.

(51) The wettability of these mixed monolayers can be related to χ_{OH}^{surf} by eq 2 if one assumes $f_{OH} = \chi_{OH}^{surf}$.

(52) When the two alkanethiols differ in chain length (C_{11} and C_{22}), the surface compositions of monolayers formed on silver and gold from solutions containing mixtures of the two thiols can differ by up to ∼40% (Laibinis, P. E.; Fox, M. A.; Folkers, J. P.; Whitesides, G. M. *Langmuir* **1991**, *7*, 3167–3173).

(53) Laibinis, P. E.; Janes, L. E.; Prime, K. L.; Nuzzo, R. G.; Whitesides, G. M. Manuscript in preparation.

(54) Balanchander, N.; Sukenik, C. *Langmuir* **1990**, *6*, 1621–1627.

(55) (a) Aschan, O. *Chem. Ber.* **1898**, *31*, 2344–2350. (b) Dobashi, Y.; Hara, S. *J. Org. Chem.* **1987**, *52*, 2490–2496.