

Oriented Surface Dipoles Strongly Influence Interfacial Wettabilities

Michael Graupe, Mitsuru Takenaga, Thomas Koini, Ramon Colorado, Jr., and T. Randall Lee*

Department of Chemistry, University of Houston
Houston, Texas 77204-5641

Received October 13, 1998

Revised Manuscript Received January 22, 1999

Hydrogen bonding between protic media and organic halides has long remained a point of controversy.^{1–6} While it is known that fluoride ions form the strongest hydrogen bonds [F⁻-H-F]⁺, there is no clear evidence establishing the hydrogen bonding of fluorine atoms covalently bound to carbon. We feel that a resolution of this controversy will likely offer insight into a variety of fields ranging from drug design, where halogens are often substituted for strongly H-bonding OH groups,^{4,5} to coatings applications, where H-bonding interactions can largely govern interfacial properties.⁷

To evaluate the degree of hydrogen bonding between fluorocarbons and protic media, we report here the wetting properties of specifically fluorinated self-assembled monolayers (SAMs) on gold. Organic thin films prepared via self-assembly are known to be highly ordered and well-defined.⁸ To probe their wetting properties, we employ contact angle measurements, which are remarkably sensitive to the chemical composition and physical structure of the outermost few angstroms of organic thin films.⁹ For our systematic study, we chose hexadecane, acetonitrile, *N,N*-dimethylformamide (DMF), water, and glycerol as contacting liquids. This combination of nonpolar (hexadecane), polar aprotic (acetonitrile and DMF), and polar protic (water and glycerol) solvents permitted us to resolve the dispersive and polar contributions to the overall interfacial properties.¹⁰

As part of the present study, we prepared SAMs from simple alkanethiols (CH₃(CH₂)_nSH with *n* = 9–15) and their CF₃-terminated analogues (CF₃(CH₂)_nSH with *n* = 9–15).¹¹ Previous studies with atomic force microscopy (AFM)¹² and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS)^{13,14} revealed that both types of films are highly ordered and similarly crystalline with indistinguishably different spacings between the headgroups. In Figure 1, we compare the advancing contact angles (θ_a) of the test liquids on the CH₃-terminated SAMs to those on the CF₃-terminated SAMs. For hexadecane, the contact angles are ca. 18° higher on the fluorinated surfaces than on the hydrocarbon surfaces. This result is not surprising and can be

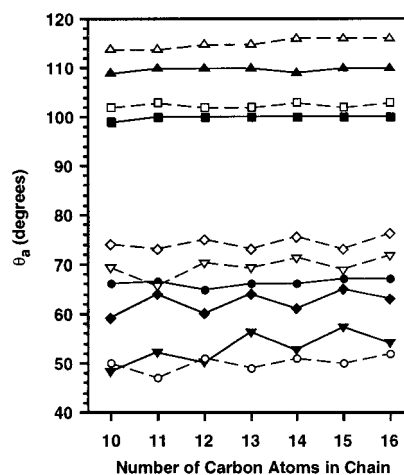


Figure 1. Advancing contact angles of hexadecane (●), acetonitrile (▼), DMF (◆), water (▲) and glycerol (■) on SAMs formed from *n*-alkanethiols (CH₃(CH₂)_nSH with *n* = 9–15; open symbols) and CF₃-terminated alkanethiols (CF₃(CH₂)_nSH with *n* = 9–15; filled symbols).

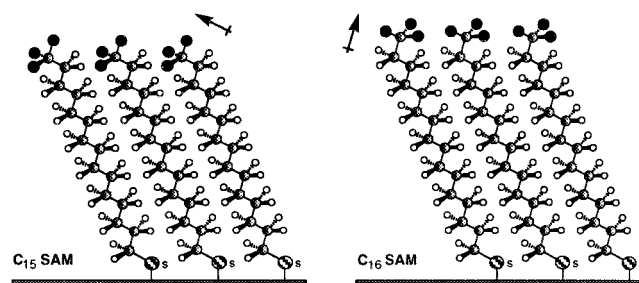


Figure 2. Illustration of the parity (or “odd-even”) effect for CF₃-terminated films.

attributed to weaker dispersive interactions between hydrocarbons and fluorocarbons than between hydrocarbons themselves.¹⁵ The contact angles for water and glycerol, however, are lower on the CF₃-terminated surfaces than on the CH₃-terminated SAMs. Initially, we could rationalize this effect by assuming the existence of hydrogen bonding between the protic liquids and the fluorine atoms at the surface.² When we examined the wettabilities of acetonitrile and DMF (Figure 1), however, we were compelled to reconsider this interpretation: the wettabilities on the CF₃-terminated surfaces are *enhanced* with these liquids, which cannot plausibly hydrogen bond.

The introduction of a terminal CF₃ group into an aliphatic hydrocarbon undoubtedly generates a strong dipole.¹⁶ Consequently, a SAM comprised of these molecules will present an ordered array of oriented dipoles that can interact with the molecular dipoles of the contacting liquid to increase the wettability. Indeed, the data in Figure 1 provide support for this model. Consider, for example, the well-established parity (“odd-even”) effect that characterizes the wettabilities of CH₃-terminated SAMs by hexadecane and is attributed to the varied orientation of the terminal functional groups relative to the surface (e.g., Figure 2), which exposes the more highly wettable methylene groups in the case of odd-numbered chains.¹⁷ Interestingly, this effect appears opposite and intensified in the wettabilities for strongly polar acetonitrile and DMF on the fluorinated surfaces. We interpret this phenomenon to reflect the strength of the dipole–dipole interactions between the liquids and the surface.

(15) Chaudhury, M. K. *Mater. Sci. Eng.* **1996**, *R16*, 97.

(16) Shafrin, E. G.; Zisman, W. A. *J. Phys. Chem.* **1957**, *61*, 1046.

(17) Tao, Y.-T. *J. Am. Chem. Soc.* **1993**, *115*, 4350.

- (1) Dixon, D. A.; Smart, B. E. *J. Phys. Chem.* **1991**, *95*, 1609.
 (2) Howard, J. A. K.; Hoy, V. J.; O’Hagan, D.; Smith, G. T. *Tetrahedron* **1996**, *52*, 12613.
 (3) Jeffrey, G. A. In *An Introduction to Hydrogen Bonding*; Oxford: New York, 1997.
 (4) Welch, J. T.; Eswarakrishnan, S. *Fluorine in Bioorganic Chemistry*; Wiley: New York, 1991.
 (5) O’Hagan, D.; Rzepa, H. S. *J. Chem. Soc., Chem. Commun.* **1997**, 645.
 (6) Thalladi, V. R.; Weiss, H.-C.; Bläser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 8702.
 (7) van Oss, C. J. In *Interfacial Forces in Aqueous Media*; Marcel Dekker: New York, 1994.
 (8) Ulman, A. In *An Introduction to Ultrathin Organic Films*; Academic: San Diego, 1991.
 (9) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
 (10) Fowkes, F. M.; Riddle, F. L., Jr.; Pastore, W. E.; Weber, A. A. *Colloids Surf.* **1990**, *43*, 367.
 (11) Graupe, M.; Koini, T.; Wang, V. Y.; Nassif, G. M.; Colorado, R., Jr.; Villazana, R. J.; Dong, H.; Miura, Y. F.; Shmakova, O. E.; Lee, T. R. *J. Fluorine Chem.* **1999**, *93*, 107.
 (12) Kim, H. I.; Koini, T.; Lee, T. R.; Perry, S. S. *Langmuir* **1997**, *13*, 7192.
 (13) Kim, H. I.; Graupe, M.; Oloba, O.; Koini, T.; Imaduddin, I.; Lee, T. R.; Perry, S. S. *Langmuir*. In press.
 (14) Colorado, R., Jr.; Graupe, M.; Takenaga, M.; Koini, T.; Lee, T. R. *Proc. Mater. Res. Soc.* Submitted for publication.

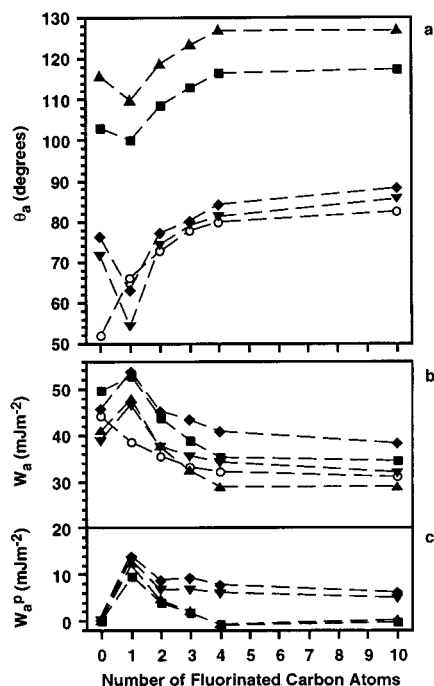


Figure 3. Variations in the interfacial properties with increasing degree of fluorination. (a) Advancing contact angles of hexadecane (O), acetonitrile (\blacktriangledown), DMF (\blacklozenge), water (\blacktriangle), and glycerol (\blacksquare) on SAMs generated from hexadecanethiols: $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$, $\text{CF}_3(\text{CH}_2)_{15}\text{SH}$, $\text{CF}_3\text{-CF}_2(\text{CH}_2)_{14}\text{SH}$, $\text{CF}_3(\text{CF}_2)_2(\text{CH}_2)_{13}\text{SH}$, $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_{12}\text{SH}$, and $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_6\text{SH}$. (b) Work of adhesion calculated from the advancing contact angles. Hexadecane (O, $\gamma_L = \gamma_L^d = 27.5 \text{ mJ m}^{-2}$) exhibits a continuous decrease in W_a with increasing degree of fluorination, whereas acetonitrile (\blacktriangledown , $\gamma_L = 29.3 \text{ mJ m}^{-2}$, $\gamma_L^d = 20.8 \text{ mJ m}^{-2}$), DMF (\blacklozenge , $\gamma_L = 36.8 \text{ mJ m}^{-2}$, $\gamma_L^d = 29.1 \text{ mJ m}^{-2}$), water (\blacktriangle , $\gamma_L = 72.8 \text{ mJ m}^{-2}$, $\gamma_L^d = 23.3 \text{ mJ m}^{-2}$), and glycerol (\blacksquare , $\gamma_L = 64.0 \text{ mJ m}^{-2}$, $\gamma_L^d = 34.3 \text{ mJ m}^{-2}$) exhibit maximum values on the CF_3 -terminated SAM. (c) Polar contributions to the work of adhesion (W_a^p) for acetonitrile (\blacktriangledown), DMF (\blacklozenge), water (\blacktriangle), and glycerol (\blacksquare).

For adsorbates consisting of even-numbered carbon atoms, the terminal dipoles are oriented nearly normal to the surface and parallel to each other (Figure 2). Because of their dense packing, they are unable to align and compensate each other. For adsorbates consisting of odd-numbered carbon atoms, however, the dipoles are tilted more parallel to the surface and can partially compensate each other. Therefore, the interaction between a polar contacting liquid will be greater for the even-numbered SAMs, which expose a greater force field at the surface, than for the odd-numbered SAMs. The question, however, still remains: is there hydrogen bonding between the fluorinated SAMs and the protic liquids?

To address this question, we examined SAMs derived from a series of hexadecanethiols having an increasing degree of fluorination ($\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ and $\text{CF}_3(\text{CF}_2)_m(\text{CH}_2)_n\text{SH}$ with $m = 0-3, 9$; $n = 15-12, 6$).¹¹ Figure 3a shows the advancing contact angles measured on these SAMs. For hexadecane, θ_a increases with increasing fluorination to a maximum value for the most highly fluorinated surface. This trend illustrates the expected decrease in dispersive interactions with increasing fluorination. For all other contacting liquids, however, θ_a shows a minimum for the $\text{CF}_3(\text{CH}_2)_{15}\text{SH}$ SAMs. As the degree of fluorination is further increased, θ_a increases again to a maximum.

From these contact angle data, we calculated the work of adhesion (W_a) between the liquids and the surfaces. The work of adhesion, which directly reflects the energy of interaction across the interface, is related to the contact angles [$W_a = \gamma_L(1 + \cos\theta_a)$] and can be separated into the sum of individual components resulting from differing interactions:^{10,18} $W_a = W_a^d + W_a^p$. The dispersive component W_a^d , which reflects only Lifshitz-van der Waals interactions, can be estimated from the dispersive com-

ponent of the surface tension of the liquid γ_L^d and the dispersive component of the surface tension of the surface γ_S^d : $W_a^d = 2(\gamma_L^d\gamma_S^d)^{1/2}$. The polar component W_a^p includes all polar interactions such as dipole-dipole and acid-base (e.g. hydrogen bonding). We estimated γ_S^d for all SAMs from the contact angle data of hexadecane ($\gamma_L = \gamma_L^d = 27.5 \text{ mJ m}^{-2}$; $W_a = W_a^d$ assumes only dispersive interactions are involved). We calculated the values of γ_L^d for the polar liquids from their contact angles on the hydrocarbon SAM. The values obtained for acetonitrile (20.8 mJ m^{-2}), DMF (29.1 mJ m^{-2}), water (23.3 mJ m^{-2}), and glycerol (34.3 mJ m^{-2}) agreed well with those reported in the literature.^{10,18} The work of adhesion (W_a) and its polar component (W_a^p) were calculated for the test liquids in contact with the SAMs (Figures 3b and 3c). The contact angle minima observed for the polar liquids on the $\text{CF}_3(\text{CH}_2)_{15}\text{SH}$ SAM correspond to maxima for W_a and W_a^p . As the degree of fluorination is further increased, the values of W_a^p decrease rapidly, approaching zero for water and glycerol. We believe that this decrease in the polar interaction is caused by an increase in the depth to which the monolayer dipole (R_H-R_F ; \rightarrow) is buried into the surface as the degree of fluorination increases.

Fowkes,¹⁰ based on work by van Oss, Chaudhury, and Good,¹⁸ showed that all interactions across an interface can be reduced to two types: dispersive and acid-base ($W_a = W_a^d + W_a^{AB}$). In this treatment, it was assumed that dipole-dipole interactions were too small to contribute significantly to the work of adhesion. Our results, however, suggest that a strong contribution to the work of adhesion arises from dipole-oriented dipole interactions W_a^{OD} . We feel that the use of a modified treatment for the work of adhesion ($W_a = W_a^d + W_a^{AB} + W_a^{OD}$) will give a more complete description of interfacial interactions.

The nonideal behavior of the dispersive interactions between hydrocarbon liquids and fluorocarbon surfaces^{15,19} should only affect a quantitative interpretation of the results presented here. Our values of γ_S^d for the fluorinated films are probably underestimated, but by no more than 4 mJ m^{-2} , which we verified by using *cis*-perfluorodecalin rather than hexadecane as the dispersive contacting liquid. The data in Figure 3 show that all polar liquids exhibit a maximum value of W_a^p on the $\text{CF}_3(\text{CH}_2)_{15}\text{SH}$ SAM; this value then decreases with increasing fluorination. If the interactions between the polar protic liquids and the fluorinated surfaces are governed by hydrogen bonding, then the values of W_a^p for these liquids should, in fact, increase with increasing fluorination, given that contacting liquids can sense buried functional groups in SAMs by penetration and/or other mechanisms.²⁰ Since, however, the oriented dipole of this SAM is positioned closest to the interface, we argue that the trends observed most likely arise from dipole-oriented dipole interactions rather than hydrogen bonding.

Before a quantitative description of the interfacial forces between fluorinated surfaces and contacting liquids can be obtained, the following issues must be resolved: (i) the true magnitude of the dispersive interactions between hydrocarbons and fluorocarbons and between polar liquids and fluorocarbons must be determined; (ii) the relationships between the polar work of adhesion and the size, shape, and dipole moment of the interacting molecules must be better understood; and (iii) the changes in lattice spacing of the SAMs that arise due to increasing the degree of fluorination must be accurately measured.

Acknowledgment. The National Science Foundation (DMR-9700662) supported this research. M.T. was on leave from Science University of Tokyo in Yamaguchi. R.C. thanks the Ford Foundation and UH CMAS for predoctoral fellowships. We also thank Professor Manoj Chaudhury for many helpful discussions.

JA983582H

(18) van Oss, C. J.; Chaudhury, M. K.; Good, R. J. *Chem. Rev.* **1988**, *88*, 927.

(19) Drummond, C. J.; Georgaklis, G.; Chan, D. Y. C. *Langmuir* **1996**, *12*, 2617.

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