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Physical organic probes of interfacial wettability reveal the importance of surface dipole effects

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ABSTRACT: The interfacial wettabilities of self-assembled monolayers (SAMs) on gold generated from trifluoromethyl- and methyl-terminated alkanethiols were evaluated using a combination of non-polar, polar protic and polar aprotic contacting liquids. The wettabilities for the non-polar hydrocarbon liquids indicate that the fluorinated films are wet less than the hydrocarbon films, demonstrating the non-ideal nature of dispersive interactions between hydrocarbons and fluorocarbons. In contrast, the wettabilities for the polar liquids revealed that the fluorinated films were wet more than the hydrocarbon films. The presence of interactions between the dipoles of the liquid molecules and oriented CF_3–CH_2 dipoles at the monolayer surface was proposed to rationalize the observed trends. Furthermore, the wettabilities of the polar aprotic liquids exhibited an inverse odd–even trend that supports the existence of oriented dipole effects upon wettability. The influence of the dipoles on the interfacial wettabilities was further examined using a series of SAMs generated from terminally fluorinated hexadecanethiols having an increasing degree of fluorination. As the dipoles were buried further into the monolayer surface, their influence on the wettabilities decreased. The interfacial energies of wetting for these films were evaluated in terms of their works of adhesion. These analyses provided evidence for the contribution of oriented dipoles to the interfacial interactions of organic thin films, in addition to the commonly recognized contributions of dispersive and acid–base interactions. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: wettability; dipole; fluorocarbon; self-assembled monolayers

INTRODUCTION

Fluorinated organic surfaces exhibit interfacial properties such as chemical inertness, water resistance and anti-adhesiveness that give rise to their widespread use in a variety of technologies.[1] For example, polytetrafluoroethylene (PTFE or Teflon), the best known fluorinated organic material, can be used as a coating that retards the biological rejection of medical implants, protects automotive components from oxidation and corrosion, and renders household cookware 'non-stick'.[1–5] The suitability of fluorinated surfaces in such a diverse range of applications has generated considerable interest in the research and development of new fluorocarbon-based materials. Progress in these efforts, however, has been limited by an inadequate understanding of the relationships between the chemical composition/structure and the interfacial properties of these materials.

During the 1950s and 1960s, Zisman and co-workers conducted the first systematic investigations of the interfacial properties of fluorinated organic materials.[6–8] These studies explored the wettability of a series of homologous *n*-alkanes on monolayers generated from the adsorption of homologous fluorinated alkanoic acids or alkylamines on metal surfaces. The wettability of a liquid on a monolayer was evaluated by measuring the advancing contact angle (θ_a) that a drop of the liquid exhibited when in contact with the surface of the solid (Fig. 1). When the cosines of the contact angles for a given monolayer were plotted against the surface tensions (γ_{LV}) of the corresponding *n*-alkane contacting liquids, a straight line of the form cos $\theta_a = m\gamma_L + b$

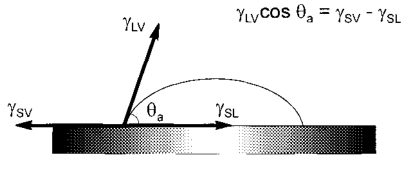

Figure 1. Schematic depiction of a drop of contacting liquid on a solid surface under an atmosphere of vapor. The relationship between the advancing contact angle (θ_a), the free energy of the liquid–vapor interface (γ_{LV}), the free energy of the solid–vapor interface (γ_{SV}), and the free energy of the solid–liquid interface (γ_{SL}) is given by Young's equation: $\gamma_{LV}\cos\theta_a = \gamma_{SV} - \gamma_{SL}$

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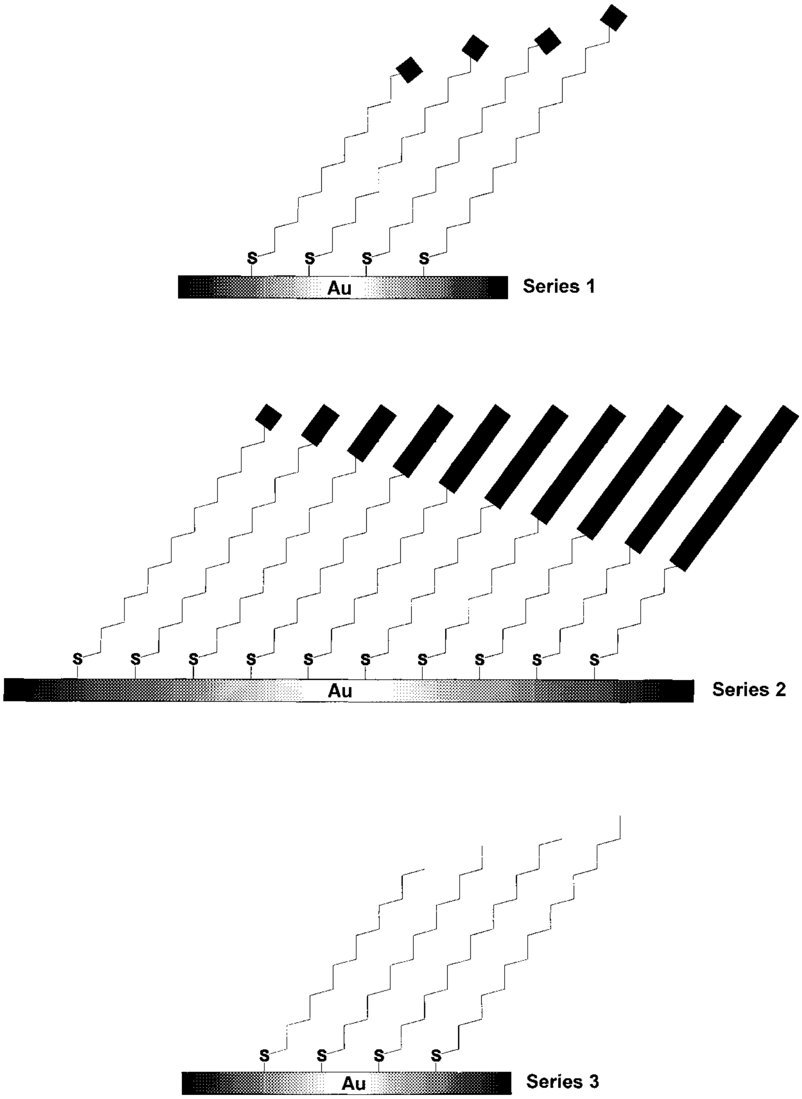

Figure 2. Illustration of SAMs on gold derived from the following series of alkanethiols: series 1, $F(CF_2)_n(CH_2)_mSH$, where $n = 1$, $m = 12$–15 (F1H*m*); series 2, $F(CF_2)_n(CH_2)_mSH$, where $n = 1$–10, $m = 15$–6 (F*n*H*m*); and series 3, $H(CH_2)_xSH$, where $x = 13$–16 (C*x*)

(where m = slope and b = y-intercept) was obtained. The x-intercept of this line with the cos $\theta_a = 1$ axis (where $\theta_a = 0°$) was defined as the critical surface tension (γ_C) of the monolayer, which was used as a measure of the surface free energy of the monolayer.[6–8] Comparison of the critical surface tensions of the fluorinated monolayers with those of analogous hydrocarbon monolayers generated from *n*-alkanoic acids and *n*-alkylamines revealed that γ_C was significantly lower on the fluorinated surfaces. Furthermore, when the critical surface tensions of the fluorinated monolayers were plotted as a function of the number of fluorinated carbon atoms per adsorbate, γ_C decreased as the number of fluorinated carbon atoms increased. Hence, Zisman was able to correlate the trends in wettability with changes in both the composition and structure of the outermost functional groups in the monolayer surface.

Although Langmuir was the first to suggest that control over the wettability and perhaps other interfacial properties (e.g. adhesion and friction) of an organic film could be achieved by selectively altering the chemical nature of the surface components,[9] Zisman's work was the first to demonstrate that the interfacial properties could be precisely controlled and quantified. Furthermore, Zisman's work stimulated a plethora of research directed toward understanding the interactions at the solid–liquid interface.[10] Nevertheless, the formulation of a detailed theoretical justification for the experimental observations was hindered by the poor characterization and limited reproducibility of *n*-alkanoic acid and *n*-alkylamine films.[6–10] Issues that have remained unresolved since Zisman's work include (1) the role of surface dipoles or hydrogen bonding on influencing interfacial wettabilities, (2) the sensitivity of contacting liquids to the presence of functional groups beneath the monolayer surface, and (3) the relationship between the packing density of the adsorbates and the wettability of the films.

To address these issues, we examined the wettabilities of two series of self-assembled monolayers (SAMs) generated from terminally fluorinated alkanethiols $F(CF_2)_n(CH_2)_mSH$ [series 1, $n = 1$, $m = 12$–15 (F1Hm); series 2, $n = 1$–10, $m = 15$–6 (FnHm)] on gold and compared them with those of SAMs generated from hydrocarbon n-alkanethiols $H(CH_2)_xSH$ [series 3, $x = 13$–16 (Cx)] on gold (see Fig. 2). Alkanethiols chemisorb readily from dilute solution onto the surface of gold substrates to form densely packed and well-ordered monolayer films.[10] Moreover, owing to the well-defined structure and oxidative inertness of the gold substrate, they can be characterized by a variety of analytical techniques.[11] In order to characterize the wetting interactions fully, we employed three different types of contacting liquids: non-polar (heptane, decane, tridecane, hexadecane, *cis*-perfluorodecalin), polar protic (water, glycerol) and polar aprotic (acetonitrile, DMF, nitrobenzene, DMSO, pyridine). Here, we use a physical organic approach to establish the relationships between the composition/structure of the films and their interfacial wettabilities.

RESULTS AND DISCUSSION

Wettabilities of terminally fluorinated SAMs

Initially, we examined the wettabilities of SAMs generated from the CF_3-terminated alkanethiols of series 1 and compared them with those of SAMs generated from the analogous CH_3-terminated n-alkanethiols of series 3.[12,13] The advancing contact angles of hexadecane, glycerol, and water were measured and evaluated as a function of the total number of carbon atoms per adsorbate (Fig. 3). Comparison of the two types of SAMs revealed the following average differences in wettability, $\Delta\theta_a = \theta_a^{CF_3} - \theta_a^{CH_3}$: 15° for hexadecane, −4° for glycerol, and −6° for water. These data suggest that, compared with the CH_3-terminated surfaces, the CF_3-terminated surfaces were wet *less* by the non-polar liquid, but wet *more* by the polar protic liquids. The results for the non-polar liquid were readily anticipated in the light of the well-known weaker dispersive interactions of fluorocarbons versus hydrocarbons.[14,15] In contrast, the results for the polar protic liquids were surprising in light of the well-known hydrophobicity of fluorocarbon films.[1] The contact-angle hysteresis, which provides a measure of surface heterogeneity,[16] was evaluated to determine if differences in surface roughness were responsible for the seemingly anomalous data.[13] The measurements, however, indicated that all of the SAM surfaces were similarly homogeneous (data not shown). Instead, we considered two phenomena that might give rise to the enhanced wettability of the polar protic liquids on the CF_3-terminated films: (1) hydrogen bonding between the polar protic liquids and the fluorine atoms of the trifluoromethyl groups and (2) attractive interactions between the permanent dipoles of the contacting polar protic molecules and oriented CF_3–CH_2 (R_F–R_H) dipoles at the surface of the SAMs.

Since surfaces consisting of highly fluorinated segments, such as perfluorocarbons, expose the same carbon-bound fluorine atoms as the CF_3-terminated SAMs, the potential for hydrogen bonding between polar protic liquids and fluorine atoms at the surface should be similar in both types of surfaces. Polar protic liquids, however, typically wet highly fluorinated surfaces less well than they wet hydrocarbon surfaces.[17] Therefore, we would not expect the contribution of hydrogen bonding to the increased wettabilities of the CF_3-terminated SAMs to be significant. To test this hypothesis, we examined the wettabilities of the CF_3- and CH_3-terminated SAMs with the polar aprotic liquid DMF, which cannot serve as a hydrogen bond donor.[18] If the increased wettabilities of

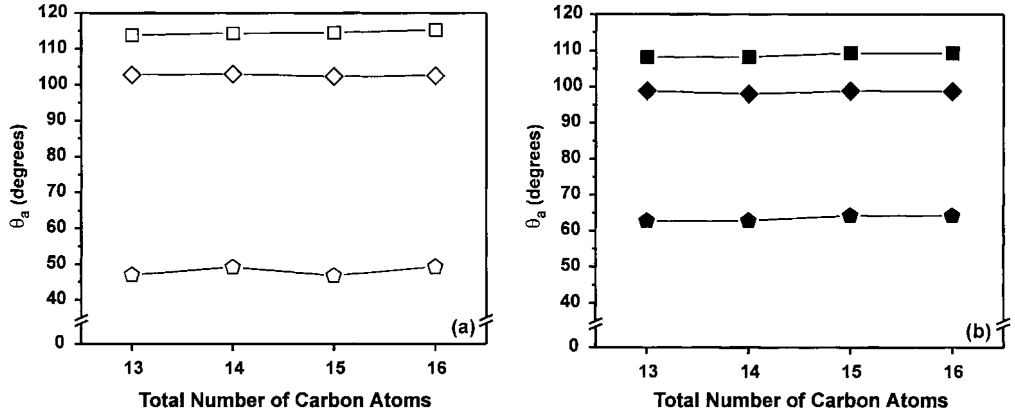

Figure 3. Advancing contact angles of hexadecane (⬠, ⬟), water (☐, ■) and glycerol (◇, ◆) on (a) CH_3-terminated SAMs of series 3 (open symbols) and (b) CF_3-terminated SAMs of series 1 (filled symbols) as a function of the total number of carbon atoms per adsorbate

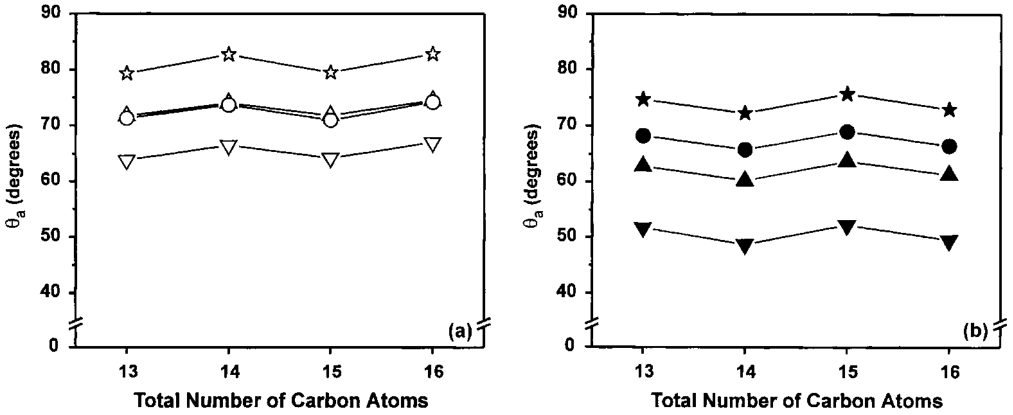

Figure 4. Advancing contact angles of DMF (△, ▲), acetonitrile (▽, ▼), nitrobenzene (○, ●) and DMSO (☆, ★) on (a) CH_3-terminated SAMs of series 3 (open symbols) and (b) CF_3-terminated SAMs of series 1 (filled symbols) as a function of the total number of carbon atoms per adsorbate

the CF_3-terminated SAMs were predominately due to hydrogen bonding, the contact angle of DMF would be expected to be higher on the fluorocarbon surfaces than on the hydrocarbon surfaces. The wettabilities of DMF on the CF_3-terminated SAMs, however, were significantly higher than on the CH_3-terminated SAMs, as indicated by an average value of $\Delta\theta_a = -13°$. These results argued against the participation of hydrogen bonding in enhancing the wettabilities of polar liquids on the CF_3-terminated SAMs.

Shafrin and Zisman proposed that the substitution of trifluoromethyl groups for the terminal methyl groups in a hydrocarbon monolayer would create an oriented force field that could interact attractively with liquid molecules.[7] Indeed, the wettabilities of DMF on our CF_3-terminated SAMs are consistent with the presence of a force field composed of oriented dipoles. Additional evidence for these oriented dipoles was provided by the observation of an odd–even (or parity) effect for the contact angles of DMF, acetonitrile, nitrobenzene and DMSO on the CF_3-terminated SAMs (Fig. 4). With regard to wettability, the odd–even effect refers to an alternation of the contact angles of a liquid on a series of monolayers as a function of the total chain length of the adsorbates.[19,20] This phenomenon is manifested in the wettabilities of hexadecane on SAMs of *n*-alkanethiols as the observation of lower contact angles on SAMs of adsorbates with an odd total number of carbon atoms (odd-numbered SAMs) than on SAMs of adsorbates with an even total number of carbon atoms (even-numbered SAMs). In the even-numbered SAMs, the terminal CH_3—CH_2 bond is oriented nearly parallel to the surface normal, thus presenting a surface that is predominately composed of methyl groups; in the odd-numbered SAMs, the terminal CH_3—CH_2 bond is tilted away from the surface normal, thus presenting a surface that is composed of methyl groups and underlying methylene groups [Fig. 5(a)]. The contact angles of hexadecane are lower on the odd-numbered SAMs because the exposure of the underlying methylene units increases the number of attractive dispersive contacts within the area of liquid drop relative to that of the even-numbered SAMs.[19–21]

We observed the odd-even effect in the wettabilities of the CH_3-terminated SAMs with hexadecane [Fig. 3(a)]. In contrast, no odd–even effect was observed for the wettabilities of the CF_3-terminated SAMs with hexadecane [Fig. 3(b)]. This result can be attributed to the larger size of a trifluoromethyl group, which apparently shields the underlying methylene group in the case of the odd-

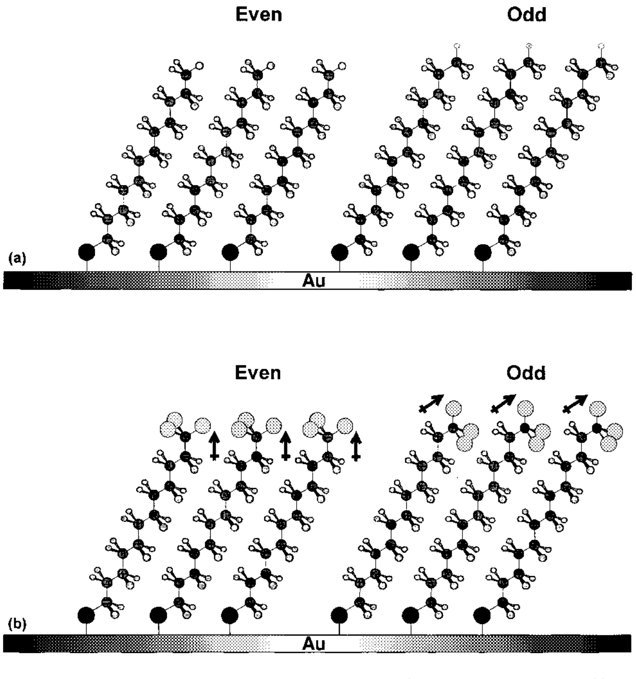

Figure 5. Schematic representation of the odd–even effect on the orientation of (a) the CH_3—CH_2 terminal bond in CH_3-terminated SAMs on gold from series 3 and (b) the CF_3—CH_2 surface dipoles in CF_3-terminated SAMs on gold from series 1. (Note: the depicted structures serve only to illustrate the relative alternation of the average terminal group orientation as a function of chain length.)

numbered SAMs, and consequently offers similar numbers of attractive dispersive contacts as the even-numbered SAMs. Glycerol and water failed to exhibit an odd–even effect on both the CH_3- and CF_3-terminated SAMs [Fig. 3(a) and (b), respectively]. These polar protic contacting liquids are highly self-associated through hydrogen bonding, which apparently renders them insensitive to small changes in the interfacial interactions. Like the wettabilities of DMF, those of acetonitrile, nitrobenzene and DMSO were all greater on the CF_3-terminated surfaces than on the CH_3-terminated surfaces. Furthermore, the wettabilities of all of the polar aprotic liquids on the CH_3-terminated surfaces exhibited an odd–even effect [Fig. 4(a)], reflecting their sensitivity to small changes in the interfacial interactions. The wettabilities on the CF_3-terminated surfaces, however, revealed a remarkably different effect [Fig. 4(b)]: the contact angles on the odd-numbered SAMs were *higher* than those on the even-numbered SAMs.

If the underlying structures of both types of monolayers are equivalent, then the terminal CF_3—CH_2 bonds in the CF_3-terminated SAMs should alternate in an manner analogous to that of the CH_3—CH_2 bonds in the CH_3-terminated SAMs. The lattice spacing and the conformational order of the monolayers were previously examined by atomic force microscopy (AFM)[22] and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS).[23] AFM images showed that the lattice spacing between trifluoromethyl and methyl groups in the respective SAMs were indistinguishable (~5.0 Å). PM-IRRAS showed that the conformational order of the underlying methylene chains in both types of monolayers were also similar, as indicated by the invariable band position of the antisymmetric methylene stretching vibration. In light of these results, we are left to consider a rationalization for the inverse odd–even effect observed on the CF_3-terminated SAMs based solely in terms of the orientation of the terminal groups [Fig. 5(b)]. The terminal CF_3—CH_2 bonds in the even-numbered SAMs are aligned nearly parallel to the surface normal, thereby presenting a vertically oriented force field that interacts strongly with the dipole moments of the contacting liquid molecules. In contrast, the tilted orientation of the terminal CF_3—CH_2 bonds in the odd-numbered SAMs aligns the dipoles of adjacent adsorbates in a head-to-tail fashion that allows them to partially compensate one another. This compensation reduces the strength of the oriented force field and consequently increases the contact angles relative to those of the even-numbered SAMs via weakened dipole–dipole interactions between the surface and the contacting liquid molecules.

Shafrin and Zisman attributed the unique wettabilities of CF_3-terminated monolayers to the presence of CF_3–CH_2 surface dipoles.[7] They proposed that replacing the trifluromethyl group with perfluoroethyl, perfluoropropyl or longer perfluoroalkyl groups would move the dipole further from the interface, and thus reduce the influence of the dipole upon the wettabilities.[8] To test this proposal, they examined the wettabilities of monolayers generated from the adsorption of terminally fluorinated alkanoic acids $F(CF_2)_n(CH_2)_mCOOH$ ($n = 2$, 3, 5, 7; $m = 16$) on chromium. As the dipole became progressively buried beneath the surface, the wettabilities of the terminally fluorinated monolayers approached those of perfluorinated monolayers, which possessed no R_F–R_H dipoles. Both the wettabilities and the critical surface tensions of the films decreased as the degree of fluorination increased.

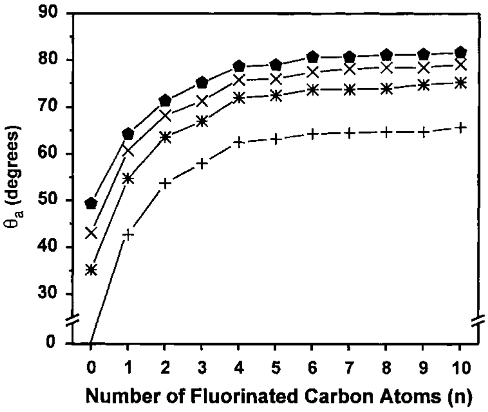

Figure 6. Advancing contact angles of heptane (+), decane (✳), tridecane (×), and hexadecane (⬟) on terminally fluorinated hexadecanethiol SAMs of series 2 as a function of the total number of fluorinated carbon atoms per adsorbate (*n*)

Motivated by Zisman's studies, we explored the effect of progressive terminal fluorination on the wettabilities of non-polar (heptane, decane, tridecane, hexadecane), polar protic (water, glycerol) and polar aprotic (acetonitrile, DMF, nitrobenzene, DMSO) contacting liquids on a series of SAMs generated from the adsorption of hexadecanethiol (C_{16}) and the series 2 terminally fluorinated hexadecanethiols on gold.[24] Figure 6 shows the advancing contact angles measured for the non-polar contacting liquids as a function of the number of fluorinated carbon atoms per adsorbate. For each liquid, the contact angle values exhibit a minimum on the CH_3-terminated SAM and steadily increase as the degree of fluorination increases. This trend suggests that the dispersive interactions between the non-polar contacting liquids and the SAMs decrease with increasing fluorination. In contrast, the contact angle values for the polar protic and polar aprotic contacting liquids exhibit minima on the CF_3-terminated SAM rather than the CH_3-terminated SAM (Fig. 7) owing to the presence of the oriented CF_3–CH_2 dipoles (see above). Moreover, as the degree of fluorination increases further, and the oriented dipole is consequently buried deeper into the monolayer surface, the contact angles of the polar liquids increase to maximum values for highly fluorinated surfaces (i.e. surfaces having more than five fluorinated carbon atoms).

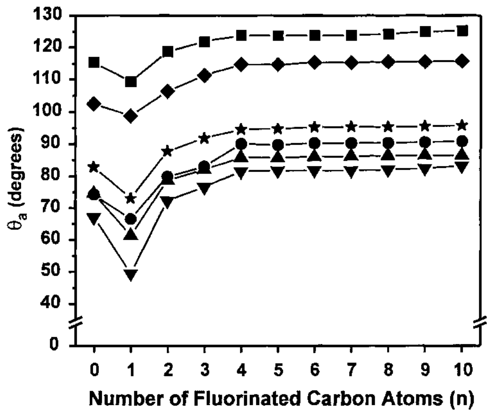

Figure 7. Advancing contact angles of water (■), glycerol (◆), DMF (▲), acetonitrile (▼), nitrobenzene (●), and DMSO (★) on terminally fluorinated hexadecanethiol SAMs of series 2 as a function of the total number of fluorinated carbon atoms per adsorbate (*n*)

By plotting the cosines of the contact angles for the non-polar contacting liquids versus the surface tensions of the contacting liquids (γ_L = 20.3 mJ m^{-2} for heptane, 23.9 mJ m^{-2} for decane, 25.9 mJ m^{-2} for tridecane and 27.5 mJ m^{-2} for hexadecane), we calculated the Zisman critical surface tensions (γ_C) of the SAMs.[6–8] Figure 8 shows γ_C as a function of the degree of fluorination for both the terminally fluorinated hexadecanethiol SAMs and Zisman's terminally fluorinated alkanoic acid monolayers. As the number of fluorinated carbon atoms increases, γ_C decreases for both types of monolayers. Despite this similarity, the following differences are noteworthy. Shafrin and Zisman reported that γ_C of the perfluoroheptyl-terminated monolayer (8.0 mJ m^{-2}) was similar to that of a perfluorooctadecanoic acid monolayer (7.9 mJ m^{-2}), and therefore, suggested that a degree of fluorination of seven carbon atoms in a film generated from terminally fluorinated adsorbates was necessary to achieve a wettability equivalent to a fully fluorinated film. In contrast, γ_C reaches a minimum value of 5.0 mJ m^{-2} on the perfluoropentyl-terminated SAM of the hexadecanethiol series and remains constant for all higher degrees of fluorination. These results suggest that the degree of terminal fluorination required to achieve the properties of complete fluorination is lower in the hexadecanethiol SAMs than in the alkanoic acid monolayers. Furthermore, the values of γ_C for the hexadecanethiol SAMs are all consistently lower that those of analogously fluorinated alkanoic acid films. We propose that these results reflect inherent differences in the crystalline order, packing density and robustness of SAMs of *n*-alkanethiols on gold versus those of monolayers generated from alkanoic acids on chromium.[6–8,10] For a given degree of fluorination, the formation of a more poorly formed film in the case of the alkanoic acid monolayers would expose underlying CF_2 groups (or CH_2 groups in the case of the CH_3- and CF_3-terminated films), which would increase the number of available attractive dispersive interactions and thus increase the value of γ_C relative to that of the alkanethiol SAMs.

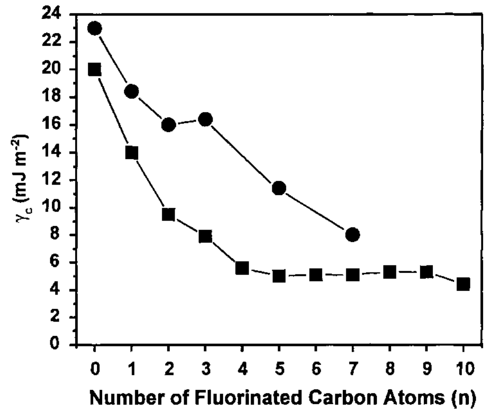

Figure 8. Critical surface tensions of Zisman's terminally fluorinated alkanoic acid monolayers (●) and terminally fluorinated hexadecanethiol SAMs of series 2 (■) as a function of the total number of fluorinated carbon atoms per adsorbate (*n*)

Evaluation of interfacial energies from wettabilities

Subsequent to Zisman's empirical correlation concerning the γ_C of a solid and the contact angles of probe liquids, many researchers have sought to develop a method for theoretically estimating the surface energy of a solid (γ_S) from contact angle data.[25] Central to all of these efforts is Young's equation:[26,27]

$$\gamma_{LV}\cos\theta_a = \gamma_{SV} - \gamma_{SL} \tag{1}$$

which relates the contact angle of a liquid in contact with a solid in an atmosphere of vapor to the free energies of the solid–vapor, liquid–vapor and solid–liquid interfaces (see Fig. 1). Zisman defined $\gamma_C = \gamma_{LV}$, when $\theta_a = 0°$.[6–8] As a result, the application of this relation to Eqn. (1) yields $\gamma_C = \gamma_{SV} - \gamma_{SL}$. Therefore, γ_C is a measure of the surface energy of a solid, but is not necessarily equal to the surface energy because γ_{SL} is not required to be zero when θ_a equals zero.

Dupré demonstrated that the work of adhesion at the solid–liquid interface is related to the free energies of the solid–vapor (γ_{SV}), liquid–vapor (γ_{LV}) and solid–liquid interfaces (γ_{SL}).[28] Equation (2)

$$W_{SL} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \tag{2}$$

shows that to separate an area of liquid from an area of solid, an area of liquid–vapor interface and an area of solid–vapor interface must be created, but an area of solid–liquid interface must be destroyed. Combining Eqns (1) and (2) yields the Young–Dupré equation:

$$W_{SL} = \gamma_{LV}(1 + \cos\theta_a) \tag{3}$$

which relates the contact angle of a liquid on a solid to the work of adhesion between the solid and liquid. With this equation, W_{SL} can be determined from the two readily measurable quantities θ_a and γ_{LV} (i.e. the surface tension of the liquid). Calculation of γ_{SV} (i.e. the surface energy of the solid) from these two quantities, however, is untenable because γ_{SL} is difficult to estimate experimentally.[25]

On the basis of Berthelot's rule for the combining of intermolecular interactions in the gas phase, Good and Girifalco proposed that W_{SL} can be expressed as the geometric mean of the component interfacial free energies, γ_{SV} and γ_{LV}:[29]

$$W_{SL} = 2\Phi(\gamma_{LV}\gamma_{SV})^{0.5} \tag{4}$$

where Φ represents a correction factor for non-ideal interactions between the solid and liquid. The value of Φ is equal to 1 when the interactions at the solid–liquid interface are entirely dispersive and of the same nature (e.g. hydrocarbon–hydrocarbon interactions). For non-ideal systems, Φ must be estimated from the molecular properties (e.g. molar volume, ionization energies) of the solid and liquids. When $\Phi = 1$, Eqns (2) and (4) can be combined to give

$$\gamma_{SL} = [(\gamma_{SV})^{0.5} - (\gamma_{LV})^{0.5}]^2 \tag{5}$$

which shows that γ_{SL} approaches zero as γ_{LV} approaches γ_{SV}. Accordingly, γ_C equals γ_{SV} only when the interactions at the solid–liquid interface are ideally dispersive. Combining Eqns (3) and (4) gives the Good–Girifalco equation:

$$\gamma_{LV}(1 + \cos\theta_a) = 2\Phi(\gamma_{LV}\gamma_{SV})^{0.5} \tag{6}$$

If Φ is known, then γ_{SV} can be estimated from θ_a and γ_{LV}. Unfortunately, the estimation of Φ requires detailed knowledge of the chemical composition of the liquids and solids, and has been shown to be highly dependent on the model used to compute it.[14]

Fowkes modified the treatment of Good and Girifalco to allow for the estimation of interfacial energies in terms of the specific interactions occurring at the solid–liquid interface.[30] His approach was based on the assumption that the surface free energy of a liquid or solid (γ) can be expressed as the sum of the energies associated with each individual type of molecular interaction occurring within the liquid or solid. For example, if molecules within a liquid or solid are subject to dispersive (γ^d), polar (γ^p), inductive (γ^i), hydrogen bonding (γ^h), and metallic bonding (γ^m) interactions, then the surface energy of the liquid or solid can be described by

$$\gamma = \gamma^d + \gamma^p + \gamma^i + \gamma^h + \gamma^m + \ldots \tag{7}$$

Additional terms may be added if other types of interactions occur within the liquid or solid.

Fowkes assumed that the interfacial energy between two surfaces $\gamma_{1,2}$ is the sum of the respective energies of each surface at the interface. If only dispersive interactions occur at the interface, the energy at surface 1 equals its total surface energy γ_1 minus the geometric mean of the dispersive components for both surfaces $(\gamma_1{}^d\,\gamma_2{}^d)^{0.5}$; likewise, the energy at surface 2 equals $\gamma_2 - (\gamma_1{}^d\,\gamma_2{}^d)^{0.5}$. The sum of the two energies yields

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - 2(\gamma_1{}^d\gamma_2{}^d)^{0.5} \tag{8}$$

which can be rearranged to give an expression for the work of adhesion between surfaces 1 and 2:

$$W_{1,2} = 2(\gamma_1{}^d\gamma_2{}^d)^{0.5} \tag{9}$$

Note that Eqn. (9) is similar to Eqn. (4), where surface 1 is a solid and surface 2 is a liquid with two exceptions: (1) no correction factor is used; and (2) the dispersive components of the solid and liquid free energies are used instead of the total solid and liquid free energies. By applying Eqn. (3), these dispersive components can be related to θ_a and γ_{LV} as

$$\gamma_{LV}(1 + \cos\theta_a) = 2(\gamma_{SV}{}^d\gamma_{LV}{}^d)^{0.5} \tag{10}$$

Equations (9) and (10) are known as the Good–Girifalco–Fowkes (GGF) equations. With these equations, the dispersive component of the free energy of a solid ($\gamma_{SV}{}^d$) can be estimated from the contact angle of a purely dispersive liquid ($\gamma_{LV} = \gamma_{LV}{}^d$). Additionally, the dispersive component of the free energy of a polar liquid (e.g. water, acetonitrile, DMSO) can be estimated from their contact angles on solids of known $\gamma_{SV}{}^d$. Furthermore, Eqn. (10) can be rearranged to reveal the following linear relation between cos θ_a and $\gamma_{LV}{}^d$:

$$\cos\theta_a = 2(\gamma_{SV}{}^d)^{0.5}(\gamma_{LV}{}^d)^{-0.5} - 1 \tag{11}$$

which demonstrates that the surface free energy of a solid is more accurately estimated by plotting cos θ_a versus $(\gamma_{LV}{}^d)^{-0.5}$, as opposed to Zisman's method of plotting it versus $\gamma_{LV}{}^d$.[14,25]

Dann, through studies of functionalized polymers, observed that for many systems involving polar liquids and/or solids, experimentally determined values of W_{SL}, calculated with Eqn. (3), were often greater than those predicted by Eqn. (9).[31,32] These observations suggested that non-dispersive interactions could also interact effectively at the interface. In light of these results, a modification to the GGF equation was offered:

$$W_{SL} = 2(\gamma_{SV}{}^{d}\gamma_{LV}{}^{d})^{0.5} + I_{SL}{}^{p} \quad (12)$$

where $I_{SL}{}^{p}$ represents contributions to the work of adhesion that arise from non-dispersive interactions, such as electrostatic, metallic, or hydrogen-bonding forces. Alternatively, this contribution can be labeled as the polar work of adhesion, denoted by $W_{SL}{}^{p}$. In the same manner, the first term in Eqn. (11) can be defined as the dispersive work of adhesion $W_{SL}{}^{d}$. Accordingly, the work of adhesion for a solid–liquid interface can be expressed as the sum of its dispersive and polar components: $W_{SL} = W_{SL}{}^{d} + W_{SL}{}^{p}$. Using Eqn. (10), we arrive at the following expression for $W_{SL}{}^{p}$:

$$W_{SL}{}^{p} = \gamma_{LV}(1 + \cos\theta_a) - 2(\gamma_{SV}{}^{d}\gamma_{LV}{}^{d})^{0.5} \quad (13)$$

Interfacial energies of terminally fluorinated SAMs

To provide additional insight into the nature of the unique wettabilities of CF_3-terminated SAMs, we calculated $W_{SL}{}^{p}$ for SAMs generated from the series of progressively fluorinated hexadecanethiols from their contact angle data.[24] As a first step, we determined the average value of $\gamma_{SV}{}^{d}$ of the non-polar SAMs generated from the *n*-alkanethiol adsorbates (Cx, where $x = 13$–16) for the purpose of using this value to estimate $\gamma_{LV}{}^{d}$ for the polar contacting liquids using Eqn. (10). The average contact angles for the non-polar hydrocarbon liquids on the non-polar CH_3-terminated SAMs were 34° for decane, 41° for tridecane, and 48° for hexadecane [heptane completely wet the methyl-terminated SAMs ($\theta_a = 0$); consequently, γ_C for these SAMs were determined from the contact angle data of the three remaining dispersive hydrocarbon liquids]. These values were used in conjunction with Eqn. (11) to calculate an average $\gamma_{SV}{}^{d} = 19.7$ mJ m^{-2}. Using $\gamma_{SV}{}^{d}$ and literature values of γ_{LV},[33] the following values of $\gamma_{LV}{}^{d}$ for the polar contacting liquids were determined, again using Eqn. (10): water, $\gamma_{LV} = 72.4$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 22.8$ mJ m^{-2}; glycerol, $\gamma_{LV} = 64.0$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 31.8$ mJ m^{-2}; DMF, $\gamma_{LV} = 36.8$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 28.7$ mJ m^{-2}; acetonitrile, $\gamma_{LV} = 27.0$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 18.6$ mJ m^{-2}; nitrobenzene, $\gamma_{LV} = 43.8$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 41.1$ mJ m^{-2}; and DMSO, $\gamma_{LV} = 43.5$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 32.0$ mJ m^{-2}. These values of $\gamma_{LV}{}^{d}$ were within ±3 mJ m^{-2} of those reported in the literature, and thus demonstrate the appropriateness of using non-polar SAMs as the dispersive solids in these calculations.[33] Values of $\gamma_{SV}{}^{d}$ for the terminally fluorinated SAMs were also calculated from Eqn. (11) using contact angles of the non-polar conatcting liquids (heptane, decane, tridecane and hexadecane; Fig. 6), which were previously used to estimate the values of γ_C in Fig. 8. Table 1 shows the contact angles and the values of $\gamma_{SV}{}^{d}$ calculated for the terminally fluorinated hexadecanethiol SAMs.

Table 1. Values of $\gamma_{SV}{}^{d}$ (mJ m^{-2}) for progressively fluorinated hexadecanethiol SAMs estimated with *n*-alkanes

F_n	$\gamma_{SV}{}^{d}$	F_n	$\gamma_{SV}{}^{d}$
F_1	14.7	F_6	9.8
F_2	12.4	F_7	9.8
F_3	11.4	F_8	9.7
F_4	10.3	F_9	9.6
F_5	10.2	F_{10}	9.5

Figure 9 shows $W_{SL}{}^{p}$, calculated from Eqn. (13), for the polar contacting liquids on the terminally fluorinated hexadecanethiol SAMs plotted as a function of the number of fluorinated carbon atoms per adsorbate. Each contacting liquid exhibits a maximum value of W_{SL} and $W_{SL}{}^{p}$ on the CF_3-terminated SAMs. These results indicate that the SAM that holds the R_F–R_H dipole closest to the interface exhibits the strongest interactions with the contacting polar liquids. As the degree of terminal fluorination increases, the values of $W_{SL}{}^{p}$ decrease, reaching constant values for degrees of fluorination above five carbon atoms. We believe that this decrease in $W_{SL}{}^{p}$ reflects the decreased polar interactions that accompany the increased depth of the R_F–R_H dipoles beneath the monolayer surface. The value of $W_{SL}{}^{p}$ equals zero for all polar contacting liquids on the CH_3-terminated SAM, indicating that only dispersive interactions are present between the liquids and the SAMs. The non-zero values of $W_{SL}{}^{p}$ for degrees of fluorination above five carbon atoms are, however, peculiar, and suggest that non-dispersive interactions

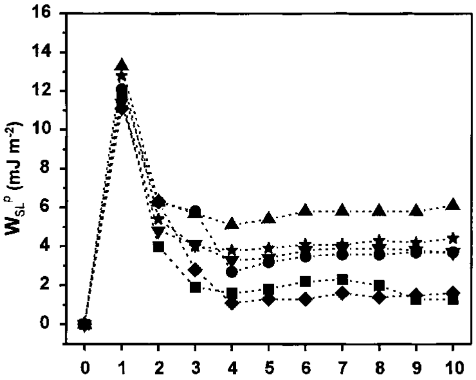

Figure 9. Polar works of adhesion, calculated using hydrocarbons as the dispersive standards, of water (■), glycerol (◆), DMF (▲), acetonitrile (▼), nitrobenzene (●), and DMSO (★) on terminally fluorinated hexadecanethiol SAMs of series 2 as a function of the total number of fluorinated carbon atoms per adsorbate (*n*)

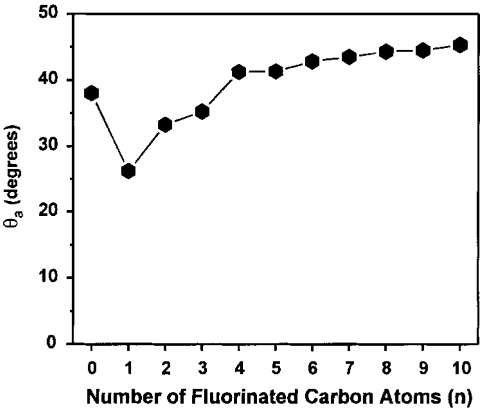

Figure 10. Advancing contact angles of *cis*-perfluorodecalin (●) on terminally fluorinated hexadecanethiol SAMs of series 2 as a function of the total number of fluorinated carbon atoms per adsorbate (*n*)

Table 2. Values of $\gamma_{SV}{}^{d}$ (mJ m^{-2}) for progressively fluorinated hexadecanethiol SAMs estimated with *cis*-perfluorodecalin

F_n	$\gamma_{SV}{}^{d}$	F_n	$\gamma_{SV}{}^{d}$
F_1	17.3	F_6	14.4
F_2	16.2	F_7	14.3
F_3	15.9	F_8	14.1
F_4	14.7	F_9	14.1
F_5	14.7	F_{10}	13.9

exist between the polar liquids and the highly fluorinated SAMs, even though the influence of the R_F–R_H dipoles has been removed. To rationalize this discrepancy, we propose that the values of $\gamma_{LV}{}^{d}$ and $\gamma_{SV}{}^{d}$ used to calculate $W_{SL}{}^{p}$ are improperly estimated owing to the non-ideal dispersive interactions between hydrocarbons and fluorocarbons.[14,15] These non-ideal interactions can plausibly give rise to the non-zero values of $W_{SL}{}^{p}$ for the highly fluorinated films.

The non-ideal dispersive interactions between hydrocarbons and fluorocarbons are apparent from their poor miscibilities.[14] Fowkes reported that values of $\gamma_{SV}{}^{d}$ for a highly fluorinated monolayer determined with Eqn. (10) using fluorocarbons as the dispersive contacting liquids were higher than those obtained using hydrocarbons.[34] Chaudhury and Whitesides directly measured the $\gamma_{SV}{}^{d}$ of hydrocarbon and fluorocarbon monolayers adsorbed on polydimethylsiloxane (PDMS) using contact deformation studies.[35,36] These authors compared the measured values to those estimated with Eqn. (10) using the contact angles of fluorocarbon and hydrocarbon liquids. The value of $\gamma_{SV}{}^{d}$ for the fluorocarbon monolayer estimated with the fluorocarbon liquid agreed with the measured value, whereas, the value obtained with the hydrocarbon liquid underestimated the measured value. Similarly, for the hydrocarbon monolayer, the value estimated with the hydrocarbon liquid agreed with the measured value, whereas, the value obtained with the fluorocarbon liquid underestimated the measured value. These results suggested that the $\gamma_{SV}{}^{d}$ of fluorocarbon monolayers would be more accurately estimated using the contact angles of fluorocarbon liquids.

Accordingly, we recalculated the values of $\gamma_{SV}{}^{d}$ for the terminally fluorinated hexadecanethiol SAMs using Eqn. (10) and the measured advancing contact angles of *cis*-perfluorodecalin (PFD, $\gamma_{LV}{}^{d} = 19.2$ mJ m^{-2}), which are plotted in Fig. 10. The alternative values $\gamma_{SV}{}^{d}$ are shown in Table 2. Conversely, we recalculated the values of $\gamma_{LV}{}^{d}$ of the polar contacting liquids with Eqn. (10) using the highly fluorinated SAM generated from $F(CF_2)_{10}(CH_2)_6SH$ (PFD-determined $\gamma_{SV}{}^{d} = 13.9$) as the dispersive solid, instead of using the *n*-alkanethiol SAMs. This treatment gave the following values: water, $\gamma_{LV} = 72.4$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 17.0$ mJ m^{-2}; glycerol, $\gamma_{LV} = 64.0$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 23.7$ mJ m^{-2}; DMF, $\gamma_{LV} = 36.8$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 27.4$ mJ m^{-2}; acetonitrile, $\gamma_{LV} = 27.0$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 16.4$ mJ m^{-2}; nitrobenzene, $\gamma_{LV} = 43.8$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 33.5$ mJ m^{-2}, and DMSO, $\gamma_{LV} = 43.5$ mJ m^{-2}, $\gamma_{LV}{}^{d} = 27.6$ mJ m^{-2}.

Figure 11 shows the values of $W_{SL}{}^{p}$ for the hexadecanethiol SAMs recalculated using the revised values of $\gamma_{LV}{}^{d}$ and $\gamma_{SV}{}^{d}$. The values of $W_{SL}{}^{p}$ for all polar liquids again exhibit maxima on the CF_3-terminated SAM. These values, however, now decrease as the degree of fluorination increases and reach constant values of zero for degrees of fluorination above five carbon atoms. We propose that for the highly fluorinated films, these data more accurately reflect the polar interactions at the interface. Specifically, polar interactions contribute to the work of adhesion when the R_F–R_H dipoles are near the surface of the monolayer. As these dipoles become buried beneath the surface with an increasing degree of fluorination, the polar contribution is reduced, ultimately

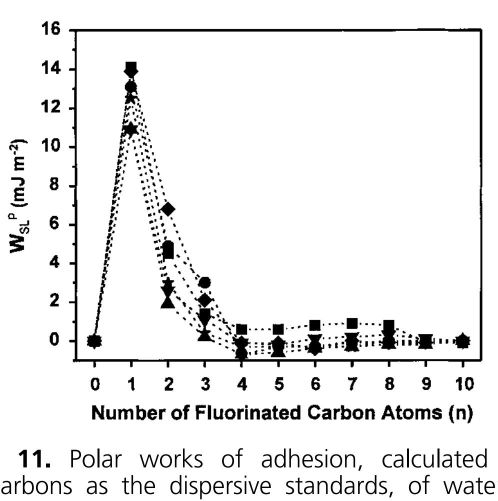

Figure 11. Polar works of adhesion, calculated using fluorocarbons as the dispersive standards, of water (■), glycerol (◆), DMF (▲), acetonitrile (▼), nitrobenzene (●), and DMSO (★) on terminally fluorinated hexadecanethiol SAMs of series 2 as a function of the total number of fluorinated carbon atoms per adsorbate (*n*)

leaving only purely dispersive interactions at the interface (for degrees of fluorination above five carbon atoms).

Based on work by Oss, Chaudhury, and Good,[37] Fowkes proposed that all interactions across an interface could be classified into two types: dispersive (e.g. hydrocarbon–hydrocarbon interactions, fluorocarbon–fluorocarbon interactions) and acid–base (e.g., hydrogen bonding, Lewis complex formation) interactions.[25,33] Consequently, the work of adhesion was expressed as $W_{SL} = W_{SL}^{d} + W_{SL}^{AB}$. This equation suggests that all polar contributions to the work of adhesion arise from acid–base interactions. The observed trends in the W_{SL}^{p} calculated for the polar protic liquids on the hexadecanethiol SAMs, however, argue against the participation of hydrogen bonding in increasing W_{SL} for the CF_3-terminated SAM. We previously argued that if hydrogen bonding between polar protic liquids and fluorine atoms at the monolayer surface were responsible for the increased wettabilities, W_{SL}^{p} would be expected to increase as the degree of fluorination increased,[23] given the observation that contacting liquids can sense buried functional groups.[38] Implicit in this argument was the assumption that the fluorine atoms in a CF_3-terminated hydrocarbon and those in a CF_3-terminated fluorocarbon have equivalent abilities to accept hydrogen bonds. Alternatively, since the polarity of the R_F–R_H bond in the CF_3-terminated hydrocarbon causes the attached fluorine atoms to become electron-rich (i.e. good Lewis bases) and the attached hydrogen atoms to become electron-poor (i.e. good Lewis acids), acid–base interactions with the contacting liquids might plausibly give rise to the observed trends in wettabilitty.

Fowkes considered the large self-association (as indicated by their immiscibilities with squalene) of certain polar aprotic liquids (e.g. DMF, acetonitrile, nitrobenzene, DMSO) to reflect the presence of both Lewis acidic and basic sites within the molecules (bifunctional liquids), which would interact to form acid–base complexes. Polar aprotic liquids that were less strongly self-associated (as indicated by their favorable miscibilities with squalene, e.g. pyridine, tetrahydrofuran, chloroform and methylene chloride) were considered to consist of molecules that contained only acidic or basic sites (monofunctional liquids), and therefore could not form intermolecular acid–base complexes. Berg showed that monofunctional liquids could interact with solid surfaces possessing monofunctional groups of complementary Lewis character to increase the work of adhesion; monofunctional liquids showed no such interaction with surfaces containing monofunctional groups of equivalent Lewis character.[25]

According to Fowkes's theories, pyridine, which is monofunctionally basic, should fail to exhibit any polar interaction with the CF_3-terminated hexadecanethiol SAM, which presents an ordered array of electron-rich CF_3 groups at the interface. The contact angle of pyridine on the CF_3-terminated hexadecanethiol SAM would be expected to be higher than that on the CH_3-terminated hexadecanethiol SAM, given their relative values of γ_{SV}^{d}. We observed, however, that the contact angle of pyridine is lower on the CF_3-terminated hexadecanethiol SAM ($\theta_a^{CF_3} = 60°$) than on the CH_3-terminated hexadecanethiol SAM ($\theta_a^{CH_3} = 70°$). Since this result fails to agree with a behavior predicted by either dispersive or acid–base interactions, it suggests that another type of interaction serves to increase the wettability on the CF_3-terminated SAM. We propose that the dipoles of the pyridine molecules interact electrostatically with the oriented R_F–R_H surface dipoles present in the CF_3-terminated SAM. Further support for this proposal is provided by the observation of an inverse odd–even effect for the wettabilities of the series 1 SAMs with pyridine (Fig. 12). Hence, the dipoles of the pyridine molecules appear to be sensitive to alternations in the strength of the electrostatic force field present at the monolayer surface.

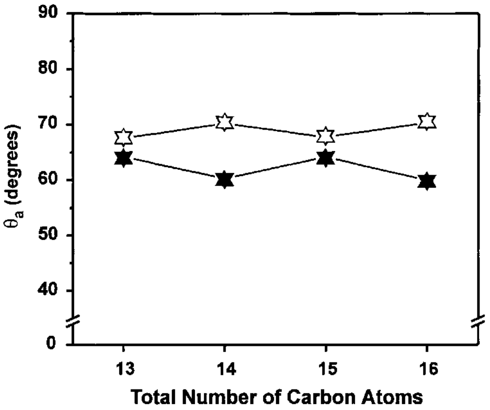

Figure 12. Advancing contact angles of pyridine (✡, ✶) on (a) CH_3-terminated SAMs of series 3 (open symbols) and (b) CF_3-terminated SAMs of series 1 (filled symbols) as a function of the total number of carbon atoms per adsorbate

On the basis of these results, we believe that Fowkes's expression for the work of adhesion, $W_{SL} = W_{SL}^{d} + W_{SL}^{AB}$, offers a useful, but limited representation of interfacial interactions. We instead feel that Dann's expression, $W_{SL} = W_{SL}^{d} + W_{SL}^{p}$, where W_{SL}^{p} is the sum of the individual types of polar contributions, such as acid–base (W_{SL}^{AB}) or electrostatic interactions (W_{SL}^{ES}), is more appropriate. Our results highlight the fact that the work of adhesion can be strongly influenced by dipole–oriented dipole interactions in cases where the surfaces possess a high degree of order. We therefore propose the inclusion of an oriented-dipole component, W_{SL}^{OD}, into the expression for W_{SL} (i.e. $W_{SL} = W_{SL}^{d} + W_{SL}^{AB} + W_{SL}^{OD}$). The W_{SL}^{OD} term represents a unique and largely neglected type of electrostatic interaction. Its inclusion in the expression for the work of adhesion will undoubtedly provide a more complete description of the interactions occurring at interfaces such as those described here.

In previous studies,[12,13,18] we estimated the polar component of the surface free energy ($\gamma_{SV}{}^p$) and the total surface free energy (γ_{SV}) of series 1 SAMs using an approach developed by van Oss *et al.*,[37] based on the extended Fowkes equation proposed by Owens and Wendt.[39] This approach assumes that $W_{SL}{}^p$ can be approximated by the geometric mean expression $2(\gamma_{SV}{}^p\ \gamma_{LV}{}^p)^{0.5}$. Both Fowkes *et al.*[33] and Berg[25] have suggested that this particular use of a geometric mean approximation is inappropriate because the manner in which a polar material interacts with other polar materials may be different than the manner in which it interacts with itself. Indeed, Dann cautioned that even though $W_{SL}{}^p$ is a function of $\gamma_{SV}{}^p$ and $\gamma_{LV}{}^p$, the relation between the two is probably complex.[32] For these reasons, we abandoned this approach and, instead, chose to express the energetics of the SAMs solely in terms of the dispersive and/or polar components of the work of adhesion.

Before a comprehensive understanding of the interfacial interactions between polar liquids and fluorinated SAMs can be achieved, the following three issues must be addressed: (1) the influence of the size, shape and dipole moment of the polar molecules in determining $W_{SL}{}^p$ must be evaluated; (2) the nature and magnitude of the non-ideal interactions between hydrocarbons and fluorocarbons must be determined; and (3) changes in the lattice spacing of the SAMs that accompany the increasing degree of fluorination must be measured. The last issue can perhaps be addressed indirectly by examining the wettabilities of the *n*-alkanes (Fig. 6) and PFD (Fig. 10) on specifically fluorinated SAMs. Future studies will explore these and related issues.

CONCLUSIONS

Studies of the wettabilities of SAMs on gold generated from CF_3-and CH_3-terminated alkanethiols revealed the following observations: (1) non-polar hydrocarbon liquids wet the CF_3-terminated surface less than the CH_3-terminated surfaces; (2) polar protic liquids wet the CF_3-terminated surfaces more than the CH_3-terminated surfaces; and (3) polar aprotic liquids also wet the CF_3-terminated surfaces more than the CH_3-terminated surfaces. The first observation was attributed to the weaker strength of hydrocarbon–fluorocarbon interactions in comparison with to hydrocarbon–hydrocarbon interactions. Initially, we proposed that either hydrogen bonding between the liquids and fluorine atoms or dipole–oriented dipole interactions between the dipoles of the liquids and those of the terminal CF_3—CH_2 bond of the adsorbates were responsible for the second observation. The third observation, however, was inconsistent with the hydrogen bonding proposal, but was compatible with the dipole-oriented dipole proposal. The observation of an inverse odd–even effect for the wettabilities of the polar protic liquids as a function of the chain length of the monolayer adsorbates provided further evidence for the dipole–oriented dipole proposal. The effect of burying the oriented dipole beneath the monolayer surface on the wettabilities was investigated by progressively increasing the number of fluorinated carbon atoms in a series of hexadecanethiol adsorbates. The wettabilities of the non-polar liquids decreased with increasing degree of fluorination owing to the increased hydrocarbon–fluorocarbon interactions. The wettabilities of the polar liquids decreased from a maximum value on the CF_3-terminated SAM with increasing degree of fluorination, reflecting an increased separation between the oriented dipole and the surface. The critical surface tensions of the SAMs were evaluated and compared with those of an analogous series of films prepared by Zisman. Although both series exhibited similar trends, the critical surface tensions of the hexadecanethiol SAMs were consistently lower than those of the analogous films, suggesting that Zisman's films were less densely packed and/or less ordered than the hexadecanethiol SAMs. We calculated polar works of adhesion for the contacting liquids on the hexadecanethiol SAMs using both hydrocarbons and a fluorocarbon liquid as the dispersive standards. Better estimates were obtained on the fluorinated SAMs when the fluorocarbon liquid was used as the standard. The polar work of adhesion was zero for the CH_3-terminated SAM, exhibited a maximum value for the CF_3-terminated SAM, and then decreased as the degree of fluorination increased. The interfacial energies of the hexadecanethiol SAMs reached constant values for degrees of fluorination above five carbon atoms. The wettability of pyridine on the CF_3-terminated SAMs indicated that dipole–oriented dipole interactions, not acid–base interactions, were responsible for the observed trends in wettability. Taken together, these results highlight the largely neglected influence of oriented dipole interactions in well-ordered interfacial systems.

EXPERIMENTAL

Materials. The contacting liquids were of the highest purity available and were used as purchased from commercial suppliers. The *n*-alkanethiols used to generate the hydrocarbon SAMs were either purchased or synthesized using common methods. The terminally fluorinated alkanethiols were synthesized using a method developed in our laboratories; the details of the syntheses are described elsewhere.[40]

Preparation of the SAMs. Ethanolic solutions of the thiols (1 mM) were prepared in glass weighing bottles, which had previously been cleaned with piranha solution (3:1 H_2SO_4/H_2O_2). ***Caution***: piranha solution reacts violently with organic materials. Substrates were prepared by the evaporation of 2000 Å of gold on to silicon wafers, which were pre-coated with a 100 Å adhesion layer of chromium. The gold-coated wafers were immersed in the thiol solutions and allowed to equilibrate for 24 h. Before characterization, the resultant SAMs were rinsed with absolute ethanol and blown dry with ultra-pure nitrogen. The compositions of the SAMs were previously verified by x-ray photelectron spectroscopy.[41]

Wettabilities of the SAMs. Contacting liquids were dispensed on the surface of the SAMs using a Matrix Technologies micro-Electrapette 25. Advancing contact angles were measured with a Ramé Hart model 100 contact angle goniometer with the pipet tip in contact with the drop. Reported values for each SAM are the average of measurements taken on at least two different slides using six drops per slide. Measured contact angles were within ±1° of the reported values. Propagating this error through the calculations, gave errors for the estimated interfacial energies of $\pm 0.3\,\mathrm{mJ\ m^{-2}}$ for γ_C $\gamma_{SV}{}^d$ and $\gamma_{LV}{}^d$ and $\pm 1.0\,\mathrm{mJ\ m^{-2}}$ for W_{SV} and $W_{SV}{}^p$.

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