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Effective van der Waals surface energy of self-assembled monolayer films having systematically varying degrees of molecular fluorination

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Abstract

The systematic variation of the van der Waals surface energy with fluorination for a series of self-assembled monolayers (SAMs) generated by the adsorption of partially fluorinated alkanethiols onto the surface of gold is examined experimentally and theoretically. The surface energy is elucidated on the basis of an effective Hamaker constant, which is obtained as a combination of the respective Hamaker constants of fluorocarbons and hydrocarbons; the fraction depends on the degree of fluorination. The good agreement between experiment and theory is discussed. In addition, the Hamaker constants of various liquids contacted on the well-defined hydrophobic surfaces are interpreted using modified Lifshitz theory.

Keywords: Self-assembled monolayer; SAM; Hydrocarbon; Fluorocarbon; Partially fluorinated; Surface energy; Hamaker constant; Lifshitz theory

1. Introduction

Interfacial properties such as wetting and friction play important roles in technological, environmental, and biological systems. Highly-ordered films that provide a useful surface for examining the interfacial properties have been fabricated by the self-assembly technique [1–4]. Notably, the wetting behavior of self-assembled monolayers (SAMs) generated by the adsorption of terminally fluorinated $CF_3(CH_2)_nSH$ molecules on gold shows some unexpected trends [5–9]. In particular, the CF_3-terminated surfaces, when compared with the non-fluorinated surfaces generated from $CH_3(CH_2)_nSH$, are less wettable in contact with non-polar liquids like hexadecane, but surprisingly more wettable in contact with polar liquids like water. The non-van der Waals energy component is significant for the CF_3-terminated surfaces in contrast to the negligibly small magnitude for the CH_3-terminated surfaces [6,8,9]. Furthermore, the friction on the terminally fluorinated SAMs is greater than that on the purely hydrocarbon SAMs [10–12].

The van der Waals interaction between macroscopic bodies can be semi-quantitatively expressed using Hamaker constants. The interaction energy per unit area (e.g., between two large planes separated at a contact distance) is proportional to the Hamaker constants and inversely proportional to the square of the contact distance. Additionally, Hamaker constants estimated using modified Lifshitz theory are evaluated from bulk properties—the permittivity and refractive index at a specific UV absorption frequency. Notably, modified Lifshitz theory has successfully elucidated the Hamaker constants of various materials, including hydrocarbons and fluorocarbons [13].

As noted above, the wettability of SAMs on gold shows an anomalous decrease in the contact angle of polar liquids upon the introduction of terminal fluorination [7–10,14]. However, as the terminal fluorination is further increased (e.g., for films derived from $CF_3(CF_2)_n(CH_2)_{12-n}SH$, where n is progressively increased from zero), the contact angle progressively increases to values greater than those of the purely hydrocarbon film. This anomaly is observed with polar probe liquids but not with non-polar hexadecane [7–10,14]. In the present study, we seek to interpret the variation of the van der Waals surface energy with fluorination. To this end, we evaluate the surface energy of the SAMs on the basis of an effective Hamaker constant,

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Table 1
The effective Hamaker constant, A_e, the calculated van der Waals surface energy, γ^{LW}(calc), and the observed van der Waals surface energy, γ^{LW}(obs), for the investigated SAMs as a function of the number of fluorinated terminal carbon atoms, N

N	A_e (10^{-20} J)	γ^{LW}(calc) (mJ/m^2)	γ^{LW}(obs) (mJ/m^2)
0	5.59	19.1	19.1
1	4.82	14.2	14.5
2	4.30	11.3	11.5
3	4.12	10.4	10.5
4	4.04	9.90	9.5
10	3.93	9.40	9.0

The use of Eq. (1) with $D = 0.180$ nm and $d = 0.127$ nm gives A_e. The relation $(\gamma^{LW}\gamma_L)^{0.5} = A_e/24\pi D^2$ with $\gamma_L = 27.5$ mJ/m^2, $D = 0.180$ nm, and each value in A_e gives γ^{LW}(calc). The modified Young–Dupre equation gives γ^{LW}(obs) from the advancing contact angle of hexadecane on the indicated surfaces.

which is calculated semi-quantitatively from a combination of the respective Hamaker constants of hydrocarbons and fluorocarbons; the fraction depends on the degree of fluorination. In addition, the Hamaker constants of various probe liquids contacted on the hydrophobic monolayer films are evaluated using modified Lifshitz theory.

2. Materials and methods

Self-assembled monolayer films generated from the partially fluorinated tridecanethiols, $CF_3(CF_2)_n(CH_2)_{12-n}SH$ with $n = 0, 1, 2, 3$ and 9, were fabricated on gold-coated silicon substrates. The SAM derived from $CH_3(CH_2)_{12}SH$ was employed as a purely hydrocarbon analogue. Note that all of the adsorbate molecules consist of the same number of carbon atoms. A Ramé–Hart contact angle goniometer was used to measure the advancing and receding contact angles of the following pure probe liquids: hexadecane, methylene iodide, glycerin, and water. The measured contact angles were reproducible to within $\pm 1°$, and the associated contact angle hysteresis values $(\theta_{adv} - \theta_{rec})$ were a consistent $10 \pm 2°$ for all films. The van der Waals surface energies were obtained using a method proposed by van Oss, Chaudhury, and Good (VCG) [15,16]. This method separates the total surface energy, γ, into two components: the Lifshitz–van der Waals interaction, γ^{LW}, and the hydrogen-bond or acid–base interaction, γ^{AB} (i.e., $\gamma = \gamma^{LW} + \gamma^{AB}$). Values of γ were estimated from advancing contact angles by use of the modified Young–Dupre equation [7–10]. Based on the assumption that hexadecane behaves as a purely dispersive liquid (i.e., having no γ^{AB} component), we then derived values of the observed van der Waals surface energy, γ^{LW}(obs), versus the number of terminally fluorinated carbons (N) for the series of fluorinated alkanethiol-based SAM films examined here (see Table 1 and Fig. 1). The non-van der Waals interactions have been described elsewhere [8,9,14].

3. Results and discussion

Fig. 1 shows the experimentally derived van der Waals surface energy, γ^{LW}(obs), for the partially fluorinated SAMs as a function of the number of fluorinated terminal carbon atoms.

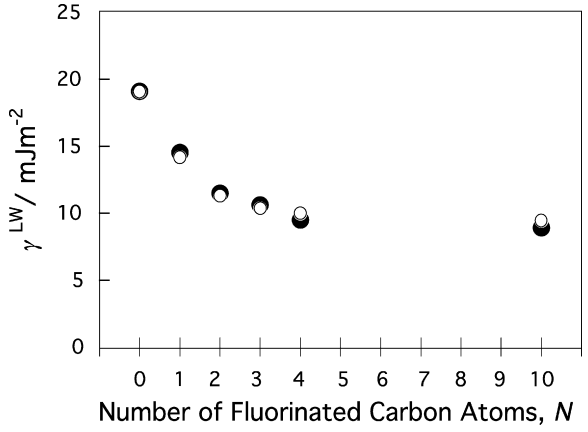

Fig. 1. Variation of the van der Waals surface energy, γ^{LW}, as a function of the number of fluorinated carbon atoms, N, for the SAMs derived from $CH_3(CH_2)_{12}SH$ ($N = 0$) and $CF_3(CF_2)_n(CH_2)_{12-n}SH$ with $n = 0, 1, 2, 3$, and 9 ($N = 1, 2, 3, 4$, and 10, respectively). The large filled circles indicate the values determined experimentally from the contact angles of hexadecane on the respective SAMs. The small hollow circles indicate the values calculated from $(\gamma^{LW}\gamma_L)^{0.5} = A_e/24\pi D^2$ with $D = 0.180$ nm and $\gamma_L = 27.5$ mJ/m^2, where A_e is the effective Hamaker constant calculated using Eq. (1).

As the degree of fluorination increases, the value of γ^{LW}(obs) steeply decreases from 19 mJ/m^2 for purely hydrocarbon films and saturates at ~9 mJ/m^2 for the partially fluorinated films. Importantly, saturation occurs at four fluorinated terminal carbons (~0.5 nm in film thickness), where the value of γ^{LW}(obs) is identical to that of the film with ten fluorinated terminal carbons (i.e., essentially perfluorinated or purely fluorocarbon). For films with four or more outer carbon atoms fluorinated, the contacting liquids sense what is essentially a perfluorinated surface, with little or no contribution from the underlying hydrocarbon component [8,9]. Consequently, the surface energy saturates for all SAMs having four or more fluorinated carbon atoms. The steep decrease and subsequent saturation in Fig. 1 reflects the molecularly controlled fluorination of the films.

We propose a theoretical model to rationalize the surface energy variation with fluorination. We assume in the model that the attractive pair potential is expressed by $-Cr^{-6}$, with the London constant represented by C and the intermolecular distance by r, and that the molecular interaction is additive. The partially fluorinated alkanethiol monolayer films, in which a layer (or layers) of fluorinated carbons is (are) stacked on the hydrocarbon bulk consisting of methylene (–CH_2–) sublayers, provides a continuous and homogeneous structure; the body continuity is approximated. The surface of the film contacts with probe liquids over a sufficiently large area, ~L^2, and the mutual surfaces are separated at a contact distance of D, which is much smaller than L. The layer/sublayer spacing is given by d, except for $d/2$ in the outermost layer. The magnitude of d is approximated by projecting the carbon–carbon bond length onto the chain axis. For simplification, no difference in molecular structure of the planar zigzag and helical conformations is considered.

Let us estimate semi-quantitatively an effective Hamaker constant, A_e, for the partially fluorinated SAMs. Integration based on the model above leads to an effective Hamaker con-