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

Mitsuru Takenaga [a,*], Sadaharu Jo [a], Michael Graupe [b], T. Randall Lee [b,*]

[a] *Department of Materials Science and Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda, Yamaguchi 756-0884, Japan*
[b] *Department of Chemistry, University of Houston, Houston, TX 77204-5003, USA*

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.
© 2008 Elsevier Inc. All rights reserved.

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,

* Corresponding authors. Faxes: +81 836 88 4564, +1 281 754 4445.
  E-mail addresses: taken@ed.yama.tus.ac.jp (M. Takenaga), trlee@uh.edu (T.R. Lee).

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.

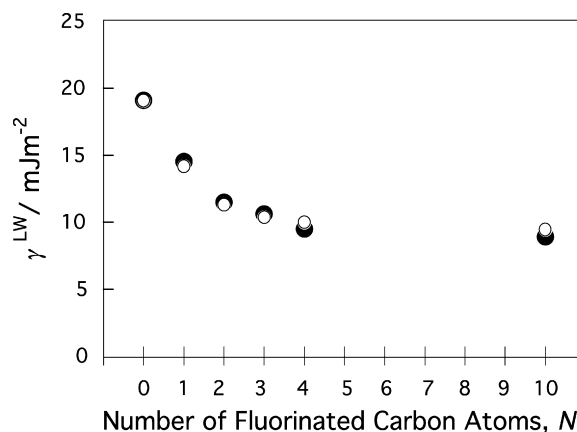Fig. 1. Variation of the van der Waals surface energy, γ^{LW}, as a function of the number of fluorinated carbon atoms, N, for the SAMs derived from CH$_3$(CH$_2$)$_{12}$SH ($N = 0$) and CF$_3$(CF$_2$)$_n$(CH$_2$)$_{12-n}$SH with $n = 0, 1, 2, 3$, and 9 ($N = 1, 2, 3, 4$, and 10, respectively). The large 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, $\sim L^2$, 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-

stant, which is expressed as a combination of the respective Hamaker constants of fluorocarbons and hydrocarbons (A_F and A_H, respectively) as shown in Eq. (1):

$$A_e = kA_F + (1-k)A_H, \qquad (1)$$

where the fluorination fraction $k = 1 - \{D/(D+f)\}^2$ with $f = (2N-1)(d/2)$ and N equal to the number of fluorinated carbon atoms. Clearly, as N goes to infinity, then $k = 1$ and A_e is equivalent to A_F; similarly, when $N = 1/2$ (or effectively zero), then $k = 0$ and A_e is equivalent to A_H. The variation of A_e with N is controlled by f, which corresponds to the thickness of the fluorocarbon layer(s). The value of D ordinarily ranges from 0.16 to 0.20 nm [17]; the magnitude should reasonably fluctuate due to the influence of particular physical characteristics of the probe liquids.

The effective Hamaker constant, A_e, was calculated from Eq. (1) by use of $D = 0.180$ nm, $d = 0.127$ nm, $A_F = 3.90 \times 10^{-20}$ J, and $A_H = 5.59 \times 10^{-20}$ J. Estimates of A_F and A_H were performed according to modified Lifshitz theory using the following values of the relative dielectric constant, ε, and refractive index, n, at an absorption frequency of 3.0×10^{15} Hz: $\varepsilon = 2.25$ and $n = 1.50$ for hydrocarbons or alkanethiol SAM films formed from alkanethiols with long alkyl chains such as $CH_3(CH_2)_{12}SH$, and $\varepsilon = 1.90$ and $n = 1.45$ for fluorocarbons. The surface energy, γ^{LW}(calc), was then calculated from each value of A_e on the basis of the relationship of $(\gamma^{LW}\gamma_L)^{0.5} = A_e/24\pi D^2$, with a dispersive surface tension for hexadecane of $\gamma_L = 27.5$ mJ/m^2 and a contact distance of $D = 0.180$ nm. Table 1 lists values of γ^{LW}(calc) versus N, together with values of A_e and γ^{LW}(obs). As illustrated in Fig. 1, the values of γ^{LW}(calc) closely track the values of γ^{LW}(obs). In particular, the curve satisfactorily mirrors such observed phenomena as the steeply decreasing behavior at $N = 1$, the approach to the perfluorinated surface at $N = 4$, and the saturation tendency at large N. The agreement between theory and experiment supports the notion that the effective Hamaker constant can play a useful role in elucidating the surface energy of partially fluorinated SAM films, and also that well-defined SAM films, when combined with non-polar hexadecane, are likely suitable for probing the van der Waals energy or dispersive surface energy of organic interfaces.

It is important to note that we analyzed the influence of fluorination on the surface energy solely on the basis of contact distance; the validity of this approach arises from the fact that the non-polar aprotic probe liquid hexadecane was utilized for all of the SAMs, which were assumed to differ only with regard to the degree of fluorination (i.e., possible differences in conformational order and/or packing density were not considered). When we employed a shorter contact distance, the overall curve in Fig. 1 shifted upward along the surface energy axis and vice versa. Apparently, the contact distance influences γ^{LW} as a fitting factor in magnitude only.

From the wetting behavior on the hydrocarbon SAM derived from $CH_3(CH_2)_{12}SH$, we obtained the dispersive surface tension of selected probe liquids [14]. We estimated the Hamaker constant, A_L(obs), from the data by using a geometric mean approximation; the values we obtained for A_L(obs)/10^{-20} J
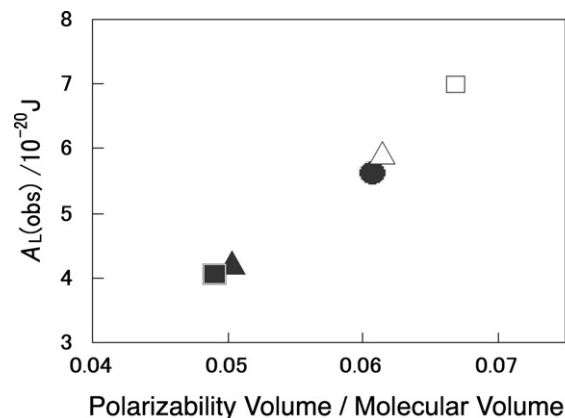

Fig. 2. Hamaker constants, A_L(obs), of the probe liquids contacted on the SAM surfaces versus the polarizability volume per molecular volume, $(\alpha/4\pi\varepsilon_0)/v$, according to the Lorenz–Lorentz equation. The numerator is the polarizability volume with vacuum permittivity ε_0, and the denominator is the molecular volume v. Values of A_L(obs) were obtained from $(\gamma_L^d \gamma)^{0.5} = (A_L A)^{0.5}/24\pi D^2$ with $\gamma = 19.1$ mJ/m^2, $A = 5.59 \times 10^{-20}$ J, $D = 0.180$ nm or 0.172 nm for water, and the dispersive component γ_L^d/mJ/m^2 for each liquid, which are: 23.3 for water (solid squares), 20.8 for acetonitrile (solid triangles), 27.5 for hexadecane (solid circles), 29.1 for DMF (open triangles), and 34.3 for glycerin (open squares) [14].

are: water 4.0, acetonitrile 4.2, hexadecane 5.6, DMF 5.9, and glycerin 7.0. The estimate was carried out using $A_H = 5.59 \times 10^{-20}$ J and $\gamma^{LW} = 19.1$ mJ/m^2 for the SAM derived from $CH_3(CH_2)_{12}SH$ and $D = 0.180$ nm for the contact distance (except for water, where $D = 0.172$ nm).

We also examined the relation between A_L(obs) and the electronic polarizability volume per molecular volume. Fig. 2 shows that the data obey the Lorenz–Lorentz equation; however, the plot of A_L(obs) versus the polarizability volume did not allow such correlation. The Hamaker constant is closely associated with the polarizability per molecular volume via the London constant, which is related to intermolecular interactions. Moreover, we calculated the Hamaker constant, A_L(calc), according to modified Lifshitz theory. The set of ε and n used for each liquid was: water, $\varepsilon = 80.4$ and $n = 1.33$; acetonitrile, $\varepsilon = 37.5$ and $n = 1.34$; hexadecane, $\varepsilon = 2.10$ and $n = 1.42$; DMF, $\varepsilon = 109$ and $n = 1.43$; and glycerin, $\varepsilon = 43.0$ and $n = 1.47$. We used an absorption frequency of 3.15×10^{15} Hz for determining A_L(calc) for all of the liquids; this value was obtained from a reasonable fit using hexadecane. The absorption frequency for several types of materials normally ranges from 2×10^{15} to 4×10^{15} Hz [17].

Fig. 3 shows a plot of A_L(obs) versus A_L(calc), together with the straight line of A_L(calc) versus A_L(calc). The significant correlation between A_L(calc) and A_L(obs) supports the validity of our treatment of the Hamaker constant both experimentally and theoretically, although some degree of error inevitably exists. As the frequency is varied, the line deviates uniformly from the plotted data; the frequency in A_L(calc) behaves as a fitting factor due to the predominant contribution of the dispersive energy term.

The exact solution for the Hamaker constant of water, which can be numerically calculated using Lifshitz theory, has been
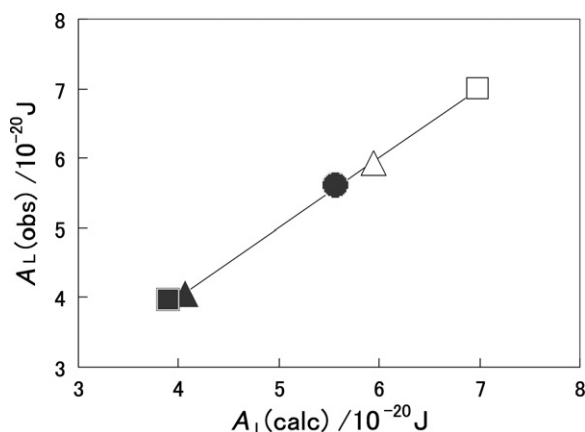
Fig. 3. Hamaker constants, A_L(obs), of the probe liquids contacted on the SAM surfaces versus the Hamaker constants calculated using modified Lifshitz theory, A_L(calc). Each symbol corresponds to the identical probe liquid in Fig. 2. The straight line is the relation of A_L(calc) versus A_L(calc) to facilitate comparison.

reported to be 4.0×10^{-20} J or 3.7×10^{-20} J [18,19]. Our data are roughly in accord with the former value. Otherwise, we can confirm for hexadecane that the van der Waals surface tension is completely governed by the London term (i.e., the dispersive surface tension) as the result of negligibly small Keesom and Debye terms.

4. Summary

The effective Hamaker constants derived here successfully rationalize the observed systematic dependence of the van der Waals surface energy on the degree of fluorination of alkanethiol-based SAMs on gold. In addition, the Hamaker constants of selected probe liquids contacted on the SAMs was evaluated using modified Lifshitz theory; the results indicate that SAMs provide reliable surfaces for the study of fundamental interfacial properties.

References

[1] M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey, J. Am. Chem. Soc. 109 (1987) 3559.
[2] L. Strong, G.M. Whitesides, Langmuir 4 (1988) 546.
[3] A. Ulman, J.E. Eilers, N. Tillman, Langmuir 5 (1989) 1147.
[4] G.-Y. Liu, P. Fenter, C.E.D. Chidsey, D.F. Ogletree, P. Eisenberger, M.J. Salmeron, Chem. Phys. 101 (1994) 4301.
[5] H.I. Kim, T. Koini, T.R. Lee, S.S. Perry, Langmuir 13 (1997) 7192.
[6] M. Graupe, T. Koini, V.Y. Wang, G.M. Nassif, R. Colorado Jr., R.J. Villazana, H. Dong, Y.F. Miura, O.E. Shmakova, T.R. Lee, J. Fluorine Chem. 93 (1999) 107.
[7] Y.F. Miura, M. Takenaga, T. Koini, M. Graupe, N. Garg, R.L. Graham, T.R. Lee, Langmuir 14 (1998) 5821.
[8] R. Colorado Jr., T.R. Lee, J. Phys. Org. Chem. 13 (2000) 796.
[9] R. Colorado Jr., T.R. Lee, Langmuir 19 (2003) 3288.
[10] M. Graupe, T. Koini, H.I. Kim, N. Garg, Y.F. Miura, M. Takenaga, S.S. Perry, T.R. Lee, Mat. Res. Bull. 34 (1999) 447.
[11] S. Li, P. Cao, R. Colorado Jr., X. Yan, I. Wenzl, O.E. Shmakova, M. Graupe, T.R. Lee, S.S. Perry, Langmuir 21 (2005) 933.
[12] J.E. Houston, C.M. Doelling, T.K. Vanderlick, Y. Hu, G. Scoles, I. Wenzl, T.R. Lee, Langmuir 21 (2005) 3926.
[13] C.J. Drummond, G. Georgaklis, D.Y.C. Chan, Langmuir 12 (1996) 2617.
[14] M. Graupe, M. Takenaga, T. Koini, R. Colorado Jr., T.R. Lee, J. Am. Chem. Soc. 121 (1999) 3222.
[15] C.J. van Oss, M.K. Chaudhury, R.J. Good, Chem. Rev. 88 (1988) 927.
[16] M.K. Chaudhury, Mater. Sci. Eng. R 16 (1996) 97.
[17] J.N. Israelachvili, Intermolecular and Surface Forces, Academic Press, San Diego, 1985.
[18] V.A. Parsegian, G.H. Weiss, J. Colloid Interface Sci. 81 (1981) 285.
[19] D.B. Hough, L.R. White, Adv. Colloid Interface Sci. 14 (1980) 3.