Odd–Even Effect in the Hydrophobicity of n-Alkanethiolate Self-Assembled Monolayers Depends upon the Roughness of the Substrate and the Orientation of the Terminal Moiety

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ABSTRACT: The origin of the odd–even effect in properties of self-assembled monolayers (SAMs) and/or technologies derived from them is poorly understood. We report that hydrophobicity and, hence, surface wetting of SAMs are dominated by the nature of the substrate (surface roughness and identity) and SAM tilt angle, which influences surface dipole/orientation of the terminal moiety. We measured static contact angles (θ) made by water droplets on n-alkanethiolate SAMs with an odd (SAMO) or even (SAME) number of carbons (average θ, range of 105.8–112.1°). When SAMs were fabricated on smooth “template-stripped” metal (MTS) surfaces [root-mean-square (rms) roughness = 0.36 ± 0.01 nm for AuTS and 0.60 ± 0.04 nm for AgTS], the odd–even effect, characterized by a zigzag oscillation in values of θ, was observed. We, however, did not observe the same effect with rougher “as-deposited” (MAD) surfaces (rms roughness = 2.27 ± 0.16 nm for AuAD and 5.13 ± 0.22 nm for AgAD). The odd–even effect in hydrophobicity inverts when the substrate changes from AuTS to AgTS (higher θ, for SAMO than SAME, with average Δθ ± (n ± 1) ≈ 3°) to AgTS (higher θ, for SAMO than SAME, with average Δθ ± (n ± 1) ≈ 2°). A comparison of hydrophobicity across AgTS and AuTS showed a statistically significant difference (Student’s t test) between SAME (Δθ, Ag evens − Au odds ≈ 5°; p < 0.01) but failed to show statistically significant differences on SAMO (Δθ, Ag odds − Au odds ≈ 1°; p > 0.1). From these results, we deduce that the roughness of the metal substrate (from comparison of MAD versus MTS) and orientation of the terminal −CH2CH3 (by comparing SAME and SAMO on AuTS versus AgTS) play major roles in the hydrophobicity and, by extension, general wetting properties of n-alkanethiolate SAMs.

INTRODUCTION

The odd–even effect is a widely observed phenomenon across many disciplines that include physics, chemistry, materials science, and biology.1–19 The odd–even effect describes an alternation in structure and/or property of an object depending upon whether there are odd or even numbers of a basic unit. In self-assembled monolayers (SAMs), the structural unit is often the number of non-hydrogen atoms, excluding the anchoring headgroup, present in the molecule that make up the monolayer (CH2 for hydrocarbons). Understanding the odd–even effect has technological implications in the design and development of SAM-based technologies, such as molecular tunneling junctions, field-effect transistors, and molecular diodes, among many others.

To design and develop technology based on SAMs, we first sought to understand the odd–even effect in simple SAMs on Au and Ag, those derived from n-alkanethiolates of medium-chain length (C9–C16). Medium-chain-length monolayers are known to be well-ordered and liquid-like, and they have been employed as model systems in several studies. Although several reports have consistently shown the odd–even effect in contact angles with liquids that wet n-alkanethiolate SAMs, there is no clear evidence of the odd–even effect in their hydrophobicity.

Figure 1a gives a summary of previously reported contact angle measurements for water on n-alkanethiolate SAMs that are relevant to the current study. Porter and co-workers reported an odd–even effect in hydrophobicity of n-alkanethiolate SAMs on Ag by measuring advancing contact angles, θadv (panel i of Figure 1a). The data by Porter and co-workers, however, were

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inconsistent with other reports that followed (Figure 1a) and did not include statistical evaluation of the data.

**HYDROPHOBICITY OF N-ALKANETHIOLATE SAMS**

Previous studies on hydrophobicity of n-alkanethiolate SAMs, as captured in the contact angle formed between the SAM and a water droplet ($\theta_{adv}$) on either Ag or Au, are not conclusive with regard to the presence or absence of an odd–even effect (Figure 1a).20,22,23,27−30 Two of the initial studies by Laibinis et al. (Whitesides’ group)20 and Walczak et al. (Porter’s group)21 are in disagreement: the former observing an odd–even oscillation in the values of the advancing contact angle, $\theta_{adv}$, while the former did not. Other studies that followed did not support the presence of an odd–even effect in the hydrophobicity of n-alkanethiolate SAMs.21−23,27−29,31−33 The odd–even effect was, however, observed with liquids that wet the SAM ($\theta < 90^\circ$) or when the thiol had a different terminal moiety besides −CH$_2$CH$_3$, for example, a terminal −CH$_2$CF$_3$. These CF$_3$-terminated n-alkanethiols have a larger dipole moment and interact more strongly with a relatively weak dipole, such as that in water, and this is enough to overcome surface roughness effects, giving rise to a measurable odd–even oscillation.9 On the basis of the smoothness and uniformity of surfaces used in Porter’s and Whitesides’ work, which were largely limited by the state-of-the-art fabrication of metal films, it is surprising that Porter and co-workers observed an odd–even effect in −CH$_2$CH$_3$-terminated n-alkanethiols. The presence of an odd–even effect was deduced from a zigzag oscillation in the contact angles but was not subjected to statistical scrutiny. In these earlier studies, there was no mention of replication, data variances, or statistical evaluation.

![Figure 1. Summary of the structure and property relevant to the wetting properties of SAMs.](https://example.com/figure1.png)

(a) Hydrophobicity of n-alkanethiolate SAMs as captured through values of advancing contact angles formed between the SAM and a drop of water as reported by (i) Porter and co-workers,14 (ii, iv, and v) Whitesides and co-workers,20 (iii) Tao and Lee,21 (vi) Colorado and Lee and Lee et al.,22,23 and (vii) Graupe et al. and Miura et al.24,25 on either Ag, Cu, or Au. All previous studies were performed on “as-deposited” surfaces. (b) Schematic illustration of the structural effect of the SAM tilt angle, because of change in the substrate, on the tilt and orientation of the terminal moiety (surface dipole) of n-alkanethiol monolayers on metal surfaces based on current generalized models of bonding and monolayer tilt angles. Orientation of the terminal moiety inverts with the change of the substrate; SAM$^{\text{Ag}}$ on Au orients like SAM$^{\text{Ag}}$ on Ag and vice versa. (c) Theoretically optimized electrostatic potential map and frontier orbital localization in n-alkanethiols as reported by Vogt.26 (d) Calculated surface normal dipole moments for n-alkanethiols bound on a metal show a significantly indifferent ($\Delta D_n - (n - 1)! \approx 0.001$) but visible odd–even oscillation.26 Graphs in panel a are reprinted with permission from (i) ref 14, Copyright 1991 American Chemical Society, (ii, iv, and v) ref 20, Copyright 1991 American Chemical Society, (iii) ref 21, Copyright 1994 Elsevier, (vi) ref 23, Copyright 2001 American Chemical Society, and (vii) ref 24, Copyright 1999 American Chemical Society.
With the importance of SAMs as a general platform in many technologies, this gap and inconsistency in one of the most basic properties of the SAMs ought to be addressed.

Current models of an ideal SAM (on an atomically flat surface and molecules in an all trans-extended conformation with no gauche rotation) suggest that an odd−even effect in wetting or other interface-dependent properties of a SAM should be expected (Figure 1b). Theoretical evaluation of the electrostatic potential maps and frontier orbital localization by Vogt does not indicate any significant electronic perturbation of molecules upon bonding to the metal that could significantly influence the interface to have a major effect and, hence, warrant significant consideration (Figure 1c). Optimized molecular dipole moments along the surface normal for Ag-based SAMs show a small zigzag oscillation (∼0.01 D) between the odd and even n-alkanethiols (Figure 1d). This difference was attributed to the change in the orientation of the terminal moiety relative to the surface and has previously been implicated as a possible origin of the odd−even effect, albeit with fluorinated SAMs.

We believe that the odd−even effect in SAMs, such as the zigzag oscillation in the surface normal dipole, should invert with the change of the substrate from Ag to Au and vice versa based on the known structures of SAMs on these surfaces (Figure 1b). Because odd−even effects have recently been observed in studies of charge transport by tunneling using physisorbed liquid top electrodes, we hypothesized

Figure 2. Surface roughness and contact angles observed with Au surfaces. AFM images of the AuTS surface: (a) two-dimensional (2D) view and (b) tilted three-dimensional (3D) view of a 3 × 3 μm surface. (e and f) Similar images for the AuAD surfaces. (c and d) Surface roughness and polycrystallinity were confirmed by SEM. Static contact angles formed by a drop of water on n-alkanethiolate SAMs formed on (d) AuTS and (h) AuAD, showing an odd−even effect only for the smoother surface.
that a similar statistically significant odd–even effect should be observed in the hydrophobicity of n-alkanethiolate SAMs. In such a case, the effect of the orientation of the terminal group and molecular packing density on the surface properties of the SAM can be deduced. These results would have consequences in application of SAMs, especially in predicting the influence of surface properties on the rate of charge injection in tunneling junctions.

Results and Discussion

All surfaces were purchased from Substrata, Inc. and were either used as received (MAD) or template-stripped (MTS) as previously described.11,19,35,36 Panels a and e of Figure 2 show atomic force microscopy (AFM) analysis of AuTS [root-mean-square (rms) roughness of 0.36 ± 0.01 nm] and AuAD (rms roughness of 2.27 ± 0.16 nm) surfaces. The observed roughness data are comparable to those previously observed by others.37,38 Average rms roughness values were obtained from at least seven substrates with 10 measurements from each substrate. Generally, AuTS surfaces have lower rms roughness and large grain sizes separated by shallow grain boundaries (panels a and b of Figure 2), making them ideal for the study of SAMs. On the other hand, AuAD surfaces, which dominated earlier studies on wetting properties of SAMs, have large rms roughness, small grain sizes, and large grain boundaries (panels e and f of Figure 2). The differences in roughness between the two surfaces were confirmed by scanning electron microscopy (SEM), which also suggests that the surfaces could be polycrystalline (panels c and g of Figure 2).

Observation of the Odd–Even Effect Depends upon Surface Roughness. The AuTS and AuAD surfaces were then used to form n-alkanethiolate [S(CH2)ₙH, where n = 8–16, except for 13] SAMs as previously described.11,19,20 When we formed n-alkanethiolate SAMs on AuTS and measured their static contact angles with water, θₛ, we observed that SAME gave higher θₛ than analogous SAMO (Figure 2d), with a characteristic zigzag oscillation with an increase in the molecular length. The data were found to be statistically significant different with a 99% confidence level using Student’s t test (p < 0.01). We also observed that, as previously observed by Laibinis et al., there is a slight but gradual increase in θₛ with an increase in the molecular length [from C₉ (107.7° ± 0.7°) to C₁₆ (112° ± 0.5°)]. When SAMs were formed on the rougher “as-deposited” (AuAD) surfaces, there is no oscillation in θₛ between the odds and evens but the gradual increase in contact angles from C₉ (105.8° ± 0.5°) to C₁₆ (109° ± 0.6°) is observed. The difference in θₛ between the shorter and longer SAMs can be attributed to the SAM becoming more rigid, giving the surface a better defined interface, or, in the case of the rough surface, the SAM starting to dictate the nature of the
than analogous SAME. Because wetting is an interface phenomenon, the analogous SAMO on Au(111) is, however, well-known that SAMs on Ag [(\(\sqrt{7} \times \sqrt{7}\))R19.1\(\theta^\circ\)] are more densely packed than those on Au [(\(\sqrt{3} \times \sqrt{3}\))R30\(\theta^\circ\)], where the surface area per adsorbed molecule is 29% larger,41,42 hence, the need to devolve the packing density from changes as a result of surface dipoles, which is the result of the orientation of the terminal group. Figure 1b shows that, for SAM\(^E\) on Au, the surface-exposed \(\text{CH}_2\text{CH}_3\) moiety is oriented almost parallel to the surface normal, analogous to SAM\(^O\) on Ag (Figure 1b). For SAM\(^O\) on Au, the terminal moiety is oriented away from the surface normal, analogous to SAM\(^E\) on Ag (Figure 1b). This reversal in orientation of the terminal moiety across the substrates is understood to be due to a change in hybridization at the headgroup from a \(S_p\) to a \(S_p\) \(9,41,43\). We therefore hypothesized that a change in the orientation of the terminal moiety, as a result of a change in the substrate, will lead to a reversal in \(\gamma\), which leads to an inversion of the odd—even effect; i.e., on Ag\(^TS\), SAM\(^O\) would have higher contact angles than SAM\(^E\), while the reverse was true with Au\(^TS\) SAMS. The Inverting Orientation of Surface Moiety Inverts the Odd–Even Effect in Hydrophobicity. Figure 3 shows our results with Ag substrates. We prepared Ag\(^TS\) and Ag\(^AD\) surfaces that showed a significant difference in roughness (rms of 0.6 ± 0.04 and 5.1 ± 0.2 nm, respectively). The observed roughness data are comparable to those previously observed by others.37,38 As previously observed, template-striped surfaces, Ag\(^TS\), had larger grains and smaller asperities than the “as-deposited”, Ag\(^AD\), surfaces.36 We, however, observe that there is a slight difference in the rms roughness between the two metal surfaces, irrespective of the method of preparation. The M\(^AD\) surfaces were the roughest and showed the largest differences (rms Ag\(^AD\) − Ag\(^TS\) = 2.86 nm), while M\(^TS\) surfaces showed a slight variation (rms Ag\(^TS\) − Ag\(^AD\) = 0.24 nm). Despite the small difference in roughness between the M\(^TS\), we believe that comparison of hydrophobicity of SAMS formed on these surfaces will give general insights into monolayers because the differences in roughness are in the order of 1.5 C–C bond length, a defect that can be mitigated by gauche effects during the assembly process. Table 1 lists the average of \(\theta_s\) for all SAMS on the two metal substrates from at least seven measurements per sample. As observed with Au surfaces, measurements of water \(\theta_s\) showed an odd—even effect in Ag\(^TS\) but not in Ag\(^AD\). When the surface is changed from Au to Ag, the odd—even effect inverts; SAM\(^O\) has a higher \(\theta_s\) than SAM\(^E\). As predicted, the odd—even effect has inverted with the change of substrate analogous to inversion in the orientation of the terminal moiety and, hence, the surface dipole. On the basis of our data, we infer that the previously reported odd—even effect in hydrophobicity of Ag SAMS was inaccurate for three reasons: (i) the differences in values of contact angles between the odds and evens for medium-sized SAMS were not subjected to any statistical test for significant differences at any confidence interval; (ii) the zigzag oscillation is analogous to what we observe in Au, suggesting that the oscillation could be due to an artifact, as previously suggested by Whitesides and co-workers,30 or an overinterpretation of the data; and (iii) with the as-deposited surface, M\(^AD\), we did not observe an odd—even effect even after repeated measurements. From the rms roughness of the Ag\(^AD\) surfaces, the asperities are too large to allow for formation of a well-defined interface upon formation of the monolayer. We, therefore, concur with Whitesides and co-workers30 that the odd—even effect reported by Porter and co-workers34 could be due to surface oxidation or adventitious impurities. To understand the origin of the difference in SAM\(^O\) and SAM\(^E\) and, hence, the odd—even effect, we examined the

| alkane
tiol (number of C) | \(\text{Au}^{TS}\) | \(\text{Au}^{AD}\) | \(\text{Ag}^{TS}\) | \(\text{Ag}^{AD}\) |
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<td>16</td>
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\(W_{\text{adh}} = \gamma(1 - \cos \theta)\)
difference in $\theta_s$ for SAMs with similar terminal group orientation (Ag odds versus Au evens and Ag evens versus Au odds) and compared these differences to SAMs whose terminal groups are oriented differently (Ag odds versus Au odds and Au evens versus Ag evens). Figure 4 gives the values of $\theta_s$ for $\text{SAM}^O$ (Figure 4a) and $\text{SAM}^E$ (Figure 4b) and a summary of all of the data (Figure 4c). We observe that contact angles derived from $\text{SAM}^O$ are statistically indistinguishable (average $\Delta \theta_{\text{Ag odds} - \text{Ag evens}} \approx 1^\circ$; Student’s $t$ test, $p > 0.1$). The small difference in $\theta_s$ indicates that its origin has a minor or no effect on the wetting properties of the SAMs. For $\text{SAM}^E$, however, we observed a statistically significant difference ($p < 0.01$) in the values of $\theta_s$ (average $\Delta \theta_{\text{Ag evens} - \text{Ag evens}} \approx 5^\circ$).

**Surface Dipole versus Packing Density.** The difference between $\text{SAM}^E$ on both substrates showed the largest difference, suggesting that this difference probably captured all factors contributing to the odd–even effect in hydrophobicity of SAMs; i.e., this is a result of an additive effect, while the small difference in $\text{SAM}^O$ is due to a subtractive effect. We hypothesized that the packing density and surface dipole, because of orientation of the terminal moiety, could account for the origin of the odd–even effect because there were no major stereoelectronic perturbations upon $n$-alkanethiols binding on the metal surface to influence surface properties. Considering SAMs with similar orientation of the terminal moiety, there is a $\sim 2^\circ$ difference in $\theta_s$ that is average $|\Delta \theta_{\text{Ag odd} - \text{Ag even}}| = |\Delta \theta_{\text{Ag even} - \text{Ag even}}| = |\Delta \theta_{\text{Ag even} - \text{Ag even}}| = \sim 2^\circ$. Because the molecular moieties on the surfaces are the same for these pairs of SAMs, one can argue that $2^\circ$ is due to the difference in the packing density. Considering hypothetical $\text{SAM}^O$ and $\text{SAM}^E$ with equal length on both substrate, the differences in values of $\theta_s$ between this pair of SAMs was calculated to be $\sim 3^\circ$. Because the orientation of the surface moiety and, hence, dipole moments change upon substituting Ag with Au, we argue that the effect of the orientation of the surface moiety is $\sim 3^\circ$, which is slightly larger than the influence of the packing density. We can therefore conclude that the odd–even effect in hydrophobicity is more influenced by the orientation of the surface moiety or surface dipoles than the packing density. Others have also observed differences in monolayer properties because of orientation of the terminal moiety.

The increase in packing density with the change of substrate from Au to Ag should make the SAM interface with water more polyethylene-like, especially for $\text{SAM}^E$. Figure 4b shows that values of $\theta_s$ are lower for AgTS than those on AuTS. This indicates a decrease in hydrophobicity and a trend toward the contact angle of polyethylene ($88 \sim 103^\circ$). A decrease in $\theta_s$ because of an increase in packing density (tending to polyethylene-like structure), however, would be mitigated by a more dominant effect if such an effect exists in these SAMs. The decrease in $\theta_s$ for $\text{SAM}^E$ occurs alongside changes in the orientation of the surface moiety, hence, surface dipole, from being along the surface normal to being tilted away from the surface normal. An analogous change, albeit in the reverse order, occurs with $\text{SAM}^O$, and as such, by comparing $\theta_s$ for $\text{SAM}^O$ on Au and Ag, we generate a set of elementary simultaneous equations (from $\text{SAM}^O$, $a + b = S^1$, and from $\text{SAM}^E$, $a - b = 1^\circ$), the solutions of which give us the contribution as a result of the packing density ($b = 2^\circ$) and effect of the surface dipole ($a = 3^\circ$). The surface dipole is therefore a more dominant effect than the change in the packing density (see Figure S1 of the Supporting Information). The effect of surface dipoles on wettability with polar liquids has previously been shown to follow a similar trend; that is, an increase in surface dipoles leads to an increase in $\theta_s$.

This paper highlights two key points relating to hydrophobicity that can be translated to wetting and other technologies relying on liquid contact with a SAM: (i) Experimental realization of the
odd—even effect in wetting, here, hydrophobicity, depends upon the quality of the surface. (ii) Surface dipoles has a more dominant effect than the packing density in SAM hydrophobicity and may account for the high $\theta_o$ relative to hydrocarbon polymers. This paper also serves to clarify the apparent ambiguity in literature data regarding hydrophobicity of SAMs.

## ASSOCIATED CONTENT

### Supporting Information

Materials and methods, schematic illustration of the effects of the packing density and charge in orientation of the surface molarity on the hydrophobicity of SAMs (Figure S1), and sample images from each SAM that we measured (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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