Packing of HO(CH$_2$)$_{14}$COOH and HO(CH$_2$)$_{15}$COOH on Graphite at the Liquid−Solid Interface Observed by Scanning Tunneling Microscopy: Methylene Unit Direction of Self-Assembly Structures

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Self-assembled monolayers (SAMs) composed of 15-hydroxypentadecanoic acid and 16-hydroxyhexadecanoic acid are investigated with scanning tunneling microscopy (STM) at the solution−graphite interface. The observed packing structures of these two molecules on the surface are dramatically different and reveal different intermolecular bonding arrangements exhibiting a new type of "odd/even" chain-length effect. In addition, solvent coadsorption has been found to occur in the case of 15-hydroxypentadecanoic acid, and an unusual surface pattern in which the molecular axes in neighboring lamellae are completely aligned with one another is observed for 16-hydroxyhexadecanoic acid.

Introduction

Though the adsorption of long-chain hydrocarbons on graphite has been known for decades,[1] initially the exact arrangement of these molecules on the surface could be deduced only from indirect techniques such as microcalorimetry, adsorption isotherm, and adsorption isobar measurements.[2] The invention of scanning tunneling microscopy (STM) by Binnig and Rohrer in 1982[3] has allowed the direct observation of self-assembled monolayers composed of alkanes and alkane derivatives at the graphite−liquid interface,[4] and a plethora of research in this field has been undertaken.[5−7] The utilization of "chemical marker groups"—functionalities such as bromine atoms or carboxylic acid groups that exhibit unusual contrast in the STM image relative to the rest of the molecule—has allowed a very precise determination of the exact position and absolute orientation of adsorbed molecules in a self-assembled monolayer at the liquid−solid interface.[8]

Observed self-assembled monolayer (SAM) patterns result from both substrate−adsorbate and adsorbate−adsorbate interactions and reflect the competition between these forces. For example, hydrogen bonding induces the self-assembly of unsubstituted fatty acids into dimers connected through their carboxylic acid functional group.[9] For n-alcohols, however, the −OH functional groups of neighboring molecules hydrogen bond in a zigzag structure extending over the whole surface domain.[10−14] The present study takes advantage of these different hydrogen-bonding connectivities by examining molecules that simultaneously contain both a carboxylic acid and an alcohol functional group. Specifically, the self-assembly of 15-hydroxypentadecanoic acid and 16-hydroxyhexadecanoic acid is investigated at the liquid−solid interface by STM. The presence of double chemical markers in a molecule, such as the alcohol and acid functional groups in these hydroxyalkane acids, greatly facilitates the understanding and interpretation of molecular conformations and surface patterning, similar to the insights gleaned from an earlier study of 12-Br-dodecanoic acid and 11-

Br-undecanoic acid, which contain bromine and carboxylic acid marker groups.[15]

The interfacial self-assembly of 15-hydroxypentadecanoic acid and 16-hydroxyhexadecanoic acid reveals several novel features in the resultant surface patterns. These molecules display a new and complex "odd/even" effect, where a change in the number of carbon atoms in the molecular chain by one subtly influences the 2D array formed at the surface. Though other odd/even effects have been previously documented in liquid crystals,[16] fatty acids,[17] and substituted fatty acids,[15] here the number of carbons in the hydroxyalkane acid backbone actually determines the intermolecular bonding patterns. Furthermore, the coadsorption of solvent molecules is affected by this odd/even phenomenon occurring only in self-assembled monolayers of 15-hydroxypentadecanoic acid and not in those of 16-hydroxyhexadecanoic acid. Coadsorption of solvent has been observed for isophthalic acid derivatives and alcohols,[18−21] and coadsorption of cosolutes has been detected in systems that contain two or more solutes,[22] but this appears to be the first case of coadsorption mediated by the odd/even effect.

Detailed, atomic-resolution studies of self-assembly patterns provide building blocks for the understanding of molecular self-organization on surfaces. These investigations pinpoint the subtle hierarchical interactions among the many different driving forces involved in self-assembly, including directional hydrogen bonding, molecule−substrate attractions, geometric constraints on individual molecules, and intermolecular interactions arising from van der Waals forces. Ultimately, a mastery of the understanding of these driving forces should lead to intelligent control and manipulation of self-assembly, an important issue in the development of future generation nanoscale electrical and mechanical devices.

Experimental Section

15-Hydroxypentadecanoic acid HO(CH$_2$)$_{14}$COOH (Lancaster, 99+%) and 16-hydroxyhexadecanoic acid HO(CH$_2$)$_{15}$COOH (Sigma, 99+%) were dissolved in 1-phenyloctane (Aldrich, 99%), 1-hexanol (Aldrich, 99+%), 1-heptanol (Aldrich, 98%),
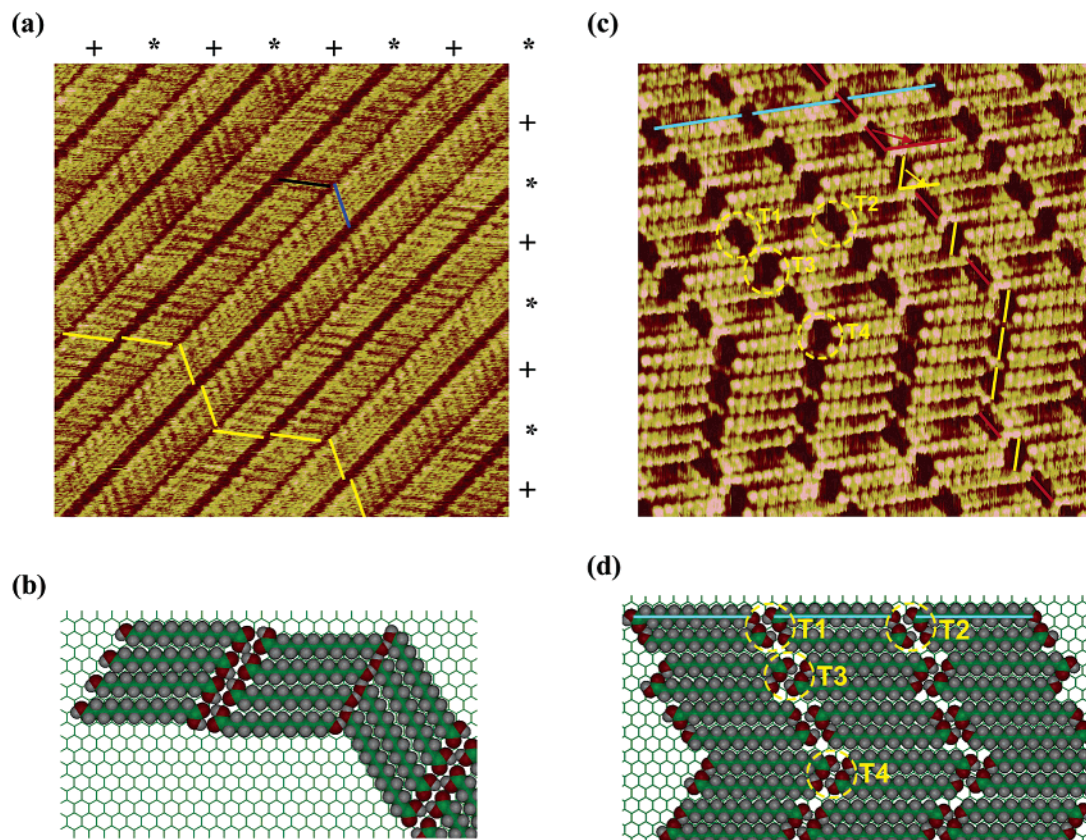
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(a)

(c)

(b)

(d)

Figure 1. (a) Constant current STM image (15 × 15 nm²) of 15-hydroxypentadecanoic acid at the interface of a 1-nonanol solution and the basal plane of graphite. This image was collected at 845 mV (sample negative) and 930 pA. One molecular length is indicated by a black or a blue bar. The asterisks (*) mark troughs that are composed of carboxylic acid dimers, and the pluses (+) mark troughs that are composed of alcohol functional groups. The yellow bars depict the global pattern, which can be described as a super-herringbone structure. (b) Top view of a computer-generated model of 15-hydroxypentadecanoic acid on a graphite surface. Green represents carbon atoms, red represents oxygen atoms, and gray represents hydrogen atoms. The molecules are positioned to register with the graphite lattice. (c) STM image of 16-hydroxyhexadecanoic acid in a 1-hexanol solution on graphite. One molecular length is indicated by one of the blue bars. These blue bars are collinear, indicating that the fatty acids occupy the same graphite lattice rows. The dark spot T1 is identical to T2 and corresponds to a tetramer of two −COOH functions and two −OH functions connected through hydrogen bonding. The red and the yellow bars depict the two different orientations observed for the dark spots. For example, T3 and T4 have the same orientation but are tilted from that of T1 and T2. The image size is 10 × 10 nm², and the imaging parameters are 800 mV (sample negative) and 1.2 nA. (d) Top view of a model of 16-hydroxyhexadecanoic acid on a graphite surface. The color scheme is the same as that for Figure 1b. Here again, the molecules are positioned to register with the graphite lattice, but it is likely that the H-donor and H-receptor groups are actually closer than depicted here to favor hydrogen bonding. T1−T4 correspond to the −COOH and −OH functional groups that are hydrogen-bonded and to the STM image in Figure 1c. Note that the orientations of T1 and T2 are identical and that T3 and T4 are identical. Furthermore, T1 and T2 are mirror images of T3 and T4.

1-octanol (Aldrich, 99+%), 1-nonanol (Fluka, ≥ 98%), 1-decanol (Aldrich, 99+%), and 1-undecanol (Aldrich, 99%) to produce nearly saturated solutions. All of these chemicals were used as received without further purification.

Samples were prepared by depositing a 10-µL droplet of solution onto the freshly cleaved basal plane of highly ordered pyrolytic graphite (HOPG) (Advanced Ceramics Corp., grade ZYB). A tip, mechanically cut from a Pt/Rh (87/13) wire (Omega Engineering Inc., 0.01-in. diameter), was immersed in the droplet. The liquid−solid interface was scanned with a Nanoscope III (Digital Instruments) STM equipped with an ∼700 × 700 nm² head.

All of the images were obtained under ambient conditions (T = 60 °F) in constant current mode. In this mode, "brighter" portions of an image correspond to a retraction of the STM tip from the sample, and "darker" portions correspond to an extension of the STM tip toward the sample. The reported tunneling currents include the offset current (often >600 pA for polar solvents such as hexanol). For presentation purposes, the images are flattened (zeroth order) by the software to normalize vertical offset. Experiments were repeated with

different tips and samples to check for reproducibility and to ensure that the images are not affected by tip or sample artifacts.

Molecular models were created with Biosym (InsightII, Molecular Simulations, Inc.) software running on a Silicon Graphics workstation.

Results

Structure of 15-Hydroxypentadecanoic Acid on Graphite. A typical STM image of a self-assembled monolayer composed of 15-hydroxypentadecanoic acid physisorbed at the graphite−nonanol interface is shown in Figure 1a. The image consists of broad lamellae where individual molecules lie along two different axes (marked by a blue and black bar) that lie at a 120° angle relative to each other. These lamellae are separated by dark troughs that have been marked with either an * or a + (the significance of these assignments is described below). The black bar in the image corresponds to one molecule oriented in an all-trans configuration lying flat on the basal plane of graphite. The measured length of a molecule that lies along a black bar is (1.9 ± 0.1) nm. The measured length of a molecule lying along a blue bar is (1.8 ± 0.1) nm. These measured

HO(CH$_2$)$_{14}$COOH and HO(CH$_2$)$_{15}$COOH on Graphite

J. Phys. Chem. B, Vol. 107, No. 1, 2003 **175**

molecular lengths are slightly shorter than the length expected for 15-hydroxypentadecanoic acid from the model, 2.07 nm. An intralamellar Moiré pattern[23] with a variation in image contrast every six to seven molecules indicates incommensurate registry between neighboring molecules and the underlying graphite lattice.

The 15-hydroxypentadecanoic acid molecule can be roughly divided into three parts: the hydroxyl function −OH, the hydrocarbon chain (CH$_2$)$_{14}$, and the carboxylic acid function −COOH. The hydrocarbon chain can be easily recognized in the STM image, for it appears as a succession of small yellow dots where each dot corresponds to one hydrogen atom. The carboxylic acid function, −COOH, is known to appear as a "dark" feature in STM images.[9] However, the hydroxyl function −OH may appear with either similar contrast or a slightly darker contrast than the hydrocarbon chain.[5] Given the similarity of these chemical markers, it is difficult to distinguish unambiguously the −COOH function from the −OH function in the molecule in these constant-current topographs (Figure 1a) and, therefore, to determine the orientation of an individual molecule from the contrast alone.

Fortunately, the relative arrangement of the molecules and, specifically, the relationship between molecular axes in neighboring lamellae can be used to determine an individual molecule's orientation. Unsubstituted fatty acid molecules physisorbed onto graphite self-assemble into interdigitated dimers that are hydrogen-bonded through carboxylic acid groups.[9,24] The angle between two such fatty acid molecules is 180°, which corresponds exactly to the angle between molecules on each side of an * trough in Figure 1a. Previous STM studies of self-assembled monolayers composed of short saturated alcohols physisorbed onto graphite[10,11,25] revealed molecules that are hydrogen-bonded through their hydrogen and oxygen atoms in the alcohol function, thereby resulting in a 120° angle between alcohol molecules in neighboring lamellae. The measured angle between the molecules on either side of the + troughs (114 ± 3)° in Figure 1a is in good agreement with the value expected for this alcohol orientation angle. The orientation of each molecule in the monolayer can therefore be assigned and is modeled in Figure 1b. Furthermore, the assignment is confirmed by the width of the troughs: (0.41 ± 0.02) nm for the troughs marked by * and (0.25 ± 0.02) nm for the ones marked by +. This difference in trough width reflects the larger space taken up by a pair of carboxylic acid functional groups compared to that of hydrogen-bonded hydroxyl functions on a surface. The measured depths of the troughs, related to the decrease in tunneling current over the particular location on the surface, are also different for the * and the + troughs. The features in the * troughs are 0.011 nm deeper than the features in the + troughs. The global pattern in Figure 1 (yellow bars) is best described as a "super-herringbone", where the classical 120° herringbone angle between two neighboring molecules is found only every second trough and molecules in immediately adjacent lamella have either a 120 or 180° angle between their axes. This structure differs from the "regular" herringbone structure exhibited by (for example) 1,12-dodecanediol, where a 120° angle is found between molecules in immediately adjacent lamellae.[10]

Structure of 16-Hydroxyhexadecanoic Acid on Graphite. A typical STM image of a monolayer composed of 16-hydroxyhexadecanoic acid physisorbed at the graphite−hexanol interface is presented in Figure 1c. One molecular length is shown with a blue bar. The measured length of a molecule is (2.08 ± 0.20) nm, slightly less than the expected value (2.19

nm) for a molecule lying flat in the all-trans configuration on the basal plane of graphite. The small bright spots, which can be distinguished within one molecule, correspond to individual hydrogen atoms protruding from the hydrocarbon chain. Large dark spots, for example, those labeled T1−T4, are found at the terminations of individual molecules and correspond to the alcohol and/or the carboxylic acid functions of the disubstituted alkanes. The shape of these dark features, which can adopt the two different orientations represented by the red and the yellow bars, is roughly rectangular. The dark spots marked by a red bar make approximately a 120° (clockwise, marked by an arrow in the Figure) angle with the molecular axis, whereas the dark spots marked by a yellow bar make approximately a 70° (clockwise, marked by an arrow in the Figure) angle with the molecular axis.

As in the case of 15-hydroxypentadecanoic acid described above, the −OH and the −COOH groups cannot be unambiguously distinguished in the STM image by contrast alone, and the absolute orientation of individual molecules is best deduced from the overall surface structure. Here, unlike the case of 15-hydroxypentadecanoic acid in nonanol (Figure 1a), all of the molecules lie along the same axis. Furthermore, the dark spots located at the ends of molecules (for example, T1 and T2) are similar in both image contrast and size. Finally, as illustrated by the blue bars, molecules in neighboring lamellae are perfectly aligned along the molecular axis. This alignment indicates that molecules in adjacent lamellae lie along the same graphite row. A model in agreement with these observed features is proposed in Figure 1d. The dark spots T1−T4 correspond to a tetramer of two hydroxyl and two carboxylic acid groups all hydrogen-bonded together. The subtle difference in the orientations of these rectangular spots with respect to the molecular axis arises from distinctions in molecular orientation on the surface. T3 differs from T1, as shown in Figure 1d, where the molecules comprising the tetramer T3 lie in an arrangement that is the mirror image of the organization of molecules comprising the tetramer T1. Though the 16-hydroxyhexadecanoic acid molecules by themselves are achiral, the molecule/surface system is two-dimensionally chiral, similar to the case of pure fatty acids on a surface,[17] leading to the distinction between the T1 and T3 moieties. There is no preference for a given molecule to adopt one two-dimensionally chiral configuration over the other, so the ratio between these two different configurations (i.e., number of red bars/number of yellow bars) is measured in different images (not shown here) to be 56:70, relatively close to the expected 1:1 value.

The orientation of the −OH group cannot be definitively identified for these molecules. The proposed cis rotamer for the alcohol functional groups shown in Figure 1d is energetically less stable in the gas phase than the trans rotamer. Nevertheless, the cis orientation allows more efficient hydrogen bonding to the pair of carboxylic acid functional groups, and thus, it is the configuration chosen here for the model. As four molecules are hydrogen-bonded to each other, the term "tetramer" will be used to describe this self-assembly pattern.

Coadsorption of 15-Hydroxypentadecanoic Acid with 1-Octanol on Graphite. Two typical STM images of monolayers composed of 15-hydroxypentadecanoic acid with coadsorbed 1-octanol physisorbed at the graphite−octanol interface are presented in Figure 2a and b. The molecular lengths of 15-hydroxypentadecanoic acid and 1-octanol are shown with blue and red bars, respectively. They are easily identified by their lengths. Aside from the molecular length differences due to the presence of the shorter octanol molecules in the fatty acid
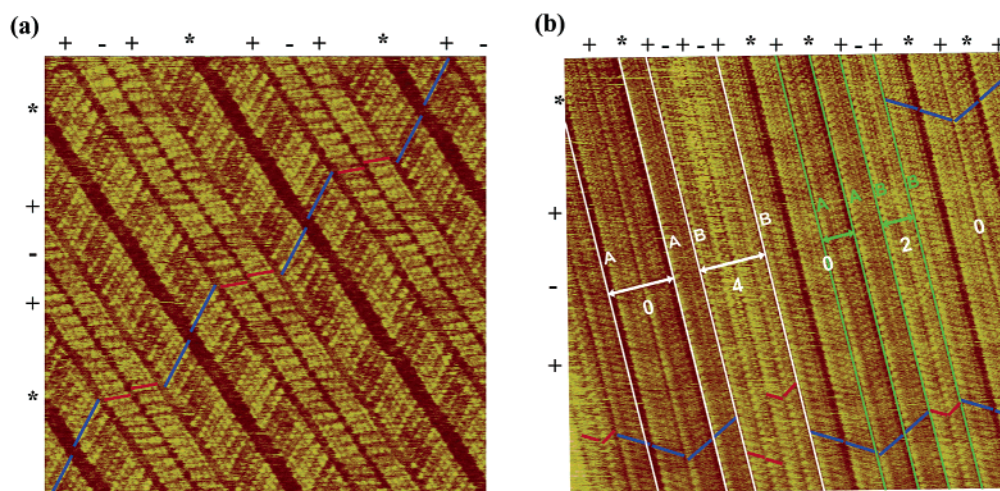
Figure 2. Constant current STM images of 15-hydroxypentadecanoic acid coadsorbed with 1-octanol at the interface of a 1-octanol solution and the basal plane of graphite. The molecular length of 15-hydroxypentadecanoic acid is indicated by a blue bar, and the molecular length of 1-octanol is indicated by a red bar. The asterisks (*) mark troughs that are composed of carboxylic acid dimers, the (+) marks troughs that are composed of alcohol functional groups (from the 15-hydroxypentadecanoic acid and from the octanol), and the minuses (−) mark troughs made up of alkane $-CH_3$ terminations of the octanol molecules. (a) As in Figure 1a, the global pattern may be described as a super-herringbone structure. The image size is 15×15 nm^2, and the imaging parameters are 840 mV (sample negative) and 690 pA. (b) The numbers 0, 2, and 4 indicate the number of octanol rows found between the lamellae made by 15-hydroxypentadecanoic acid dimers. The green B lines frame two rows of octanol molecules, and the green A lines frame one row of 15-hydroxypentadecanoic acid molecules. The green arrows both have the same length. The white B lines frame four rows of octanol molecules, and the white A lines frame two rows of 15-hydroxypentadecanoic acid molecules. The white arrows both have the same length. The octanol molecules present two different self-assembly patterns (forming a herringbone or a collinear structure). The image size is 25×25 nm^2, and the imaging parameters are 920 mV (sample negative) and 350 pA.

monolayer, the global pattern in Figure 2a is similar to the pattern in Figure 1a and may be once again described as a super-herringbone structure.

The identification of the absolute orientation of the molecules inside the lamella in Figure 2a is again facilitated by a close examination of molecular axis/lamellar axis angles. The * marks troughs between collinear fatty acid molecules composed of carboxylic acid dimers. The + marks troughs between alcohol functional groups (of an octanol molecule and a 15-hydroxypentadecanoic acid molecule) where the two molecular axes on either side of the + trough are 120° with respect to each other. The −OH functional groups, connected by −OH···HO− hydrogen bonding, tie rows of solute molecules together with rows of solvent molecules. The − marks troughs terminated by the alkane $-CH_3$ groups of two octanol molecules. In comparison to Figure 2a, Figure 2b depicts a different, more complex domain for this 2D film. In this domain, different arrangements of the molecular rows are present in the same region of the surface. In some cases, no molecules of octanol are found between the hydroxyl functions of the solute molecules, whereas two or four rows of octanol molecules are found in other cases, as indicated by the white numbers in Figure 2b.

Discussion

New Odd/Even Effect. The structure of self-assembled monolayers on a graphite surface results from the optimization of surface−adsorbate and adsorbate−adsorbate interactions. The latter consists essentially of both lateral van der Waals interactions between molecular chains and intermolecular hydrogen bonding between hydrogen donors and hydrogen receptors (carboxylic acids, amines, or alcohols). Monolayers formed by 15-hydroxypentadecanoic acid and by 16-hydroxyhexadecanoic acid show dramatically different surface assembly patterns, which are very unlikely to arise from nonspecific van der Waals interactions. Indeed, the hydrocarbon backbone is increased in length by only 7.7% when the $(CH_2)_n$ chain is changed from

13 to 14 carbon atoms. This leads to only a small change in the energetics of the overall surface structure due to contributions from van der Waals interactions between hydrocarbon chains. The observed differences in the monolayer surface structure for these two species can, however, be nicely explained by an odd/even length effect. As illustrated by the arrows in Figure 3a and b, if the carboxylic acid groups of 15- and 16-hydroxyacid molecules have the same orientation, then the terminal alcohol groups must be directed differently with respect to the hydrocarbon chain. This point is particularly important since alcohol groups are known to contribute significantly to intermolecular interactions through hydrogen bonding. Consequently, patterns where such hydrogen bonds can be formed are more likely to lead to stable monolayers of physisorbed molecules.

In the present case, molecules with an odd number of carbon atoms support a structure where the −OH terminations are in a favorable orientation (see Figure 3a) to connect to the −OH groups of molecules in neighboring rows, resulting in the structure shown in the STM image of Figure 1a with the corresponding model in Figure 1b. However, molecules with an even number of carbon atoms (Figure 3b) would have an organization of alcohol terminations where a methylene hydrogen lies between the two hydroxyl groups (this methylene position is marked by the large black * in Figure 3b), thereby creating an unfavorable situation for intermolecular hydrogen bonding. To avoid frustrating such hydrogen bonding through the end hydroxyl groups in chains with an even number of carbon atoms, the pattern observed in Figure 1c and schematically represented in Figures 1d and 3c is preferred. In essence, this arrangement switches the side-by-side configuration from the head-to-head structure (observed for 15-hydroxypentadecanoic acid) to a head-to-tail arrangement (observed for 16-hydroxyhexadecanoic acid).

This appears to be the first example in which an additional methylene unit in the carbon chain of a functionalized fatty acid is found to change the bonding structure between molecules forming a monolayer. Unlike previously known odd/even
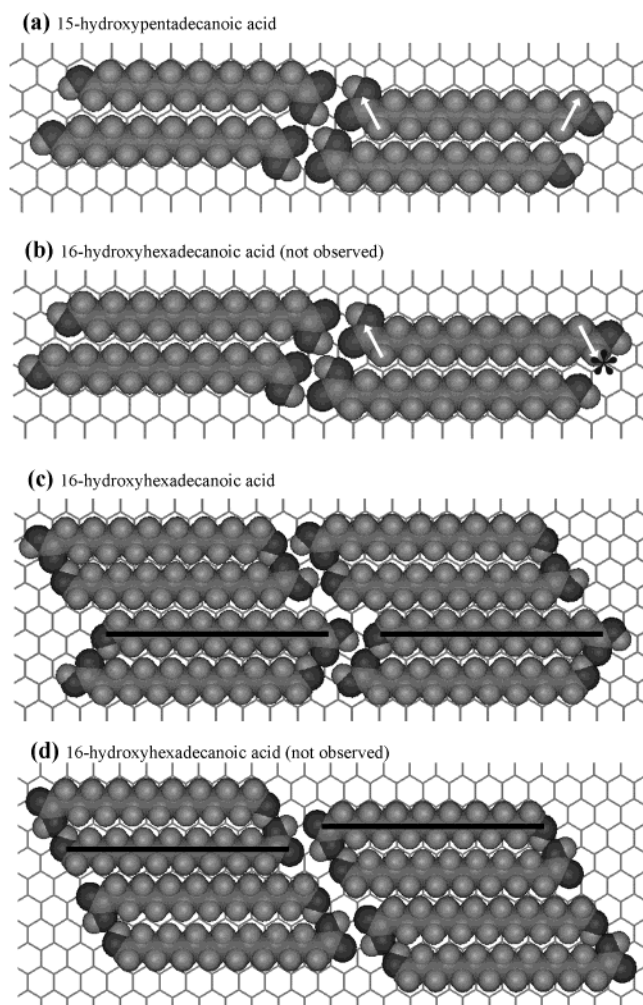
HO(CH$_2$)$_{14}$COOH and HO(CH$_2$)$_{15}$COOH on Graphite

J. Phys. Chem. B, Vol. 107, No. 1, 2003 **177**

(a) 15-hydroxypentadecanoic acid

(b) 16-hydroxyhexadecanoic acid (not observed)

(c) 16-hydroxyhexadecanoic acid

(d) 16-hydroxyhexadecanoic acid (not observed)

Figure 3. Top views of models describing a similar arrangement of four molecules of (a) 15-hydroxypentadecanoic acid and (b) four molecules of 16-hydroxyhexadecanoic acid on a graphite surface. In these arrangements, the carboxylic acid functional groups have a similar orientation, but because of the odd/even number of carbon atoms in the molecular chains shown in (a) and (b), the −OH terminal groups point in different directions, as illustrated by the white arrows. (a) The alcohol functionalities of the two right-hand molecules are in a favorable orientation to hydrogen bond with alcohol functionalities from adjacent lamellae to give the pattern shown in Figure 1b. (b) The alcohol functionalities of the two right-hand molecules are in an unfavorable orientation (because a methylene hydrogen, marked by the black asterisk, lies between the two hydroxyl groups) and cannot hydrogen bond with alcohol functionalities from adjacent lamellae. This structure has not been observed in STM images in the present study. Top views of models describing a similar arrangement of eight molecules of 16-hydroxyhexadecanoic acid where one orientation (c) shows the molecular axes in neighboring lamellae aligned, as portrayed by the black bars. (d) Molecular axes in neighboring lamellae are offset, again portrayed by superimposed black bars. The orientation of the carboxyl groups in (c) corresponds to a 45° hydrogen bond direction/molecular axis angle configuration whereas that in (d) corresponds to a 25° hydrogen bond direction/molecular axis angle configuration on the graphite surface. In (c), the chemical functionalities −OH and −COOH are close to each other, forming a densely packed tetramer of hydrogen-bonded H-donor and H-receptor groups. In (d), as the chemical functionalities −OH and −COOH are far from each other in this model, the stabilization of the monolayer through hydrogen bonding is compromised. This structure has not been observed in STM images in the present study.

effects,[11,19,20] the number of atoms in the hydrocarbon chain here determines not only the surface pattern but also molecular bonding partners. This self-assembly phenomenon

TABLE 1: Patterns Observed by STM for Self-Assembled Monolayers Physisorbed onto Graphite from Different Solutions

solvent ↓	solute →	15-hydroxypenta-decanoic acid[a]	16-hydroxyhexa-decanoic acid[a]
hexanol		−	tetramer[b]
heptanol		super-herringbone[b]	tetramer[b]
octanol		super-herringbone[b] + solvent coadsorption	tetramer[b]
nonanol		super-herringbone	tetramer[b]
decanol		decanol[c]	decanol[c]
undecanol		undecanol[c]	undecanol[c]
phenyloctane		super-herringbone[b]	−

[a] All solutions are at or near saturation with solute. [b] The terms super-herringbone and tetramer refer to the self-assembly patterns formed on the surface by solute and are described more fully in the Results section. The singular case of 15-hydroxypentadecanoic acid with octanol revealed coadsorption of octanol into the self-assembled monolayer. A minus sign (−) indicates that no ordered STM image was observed. [c] Surface structures containing only the solvent were observed and were typical of the patterns formed by short-chain alcohols.

has its origin in both the position and the nature of the chemical functional group involved in the intermolecular bonding. The odd/even effect observed by Fang[15] for Br(CH$_2$)$_{10}$COOH and Br(CH$_2$)$_{11}$COOH did not involve a change in the intermolecular bonding structure because the bonding constraints inherent in Br···Br van der Waals attractions do not necessitate such a rearrangement when the number of CH$_2$ units is changed. The directional specificity of the hydrogen bonding, which itself is strongly dependent on the orientation of the methylene group to which −OH is bonded, is, therefore, a key factor in determining the 2D monolayer structure observed in the present study.

Solvent Coadsorption. This new odd/even effect has interesting consequences for solvent coadsorption. Since all the 15-hydroxypentadecanoic acid molecules have the same absolute orientation within a lamella, all of the hydroxyl functions are on the same side of a lamella, and coadsorption of solvent alcohol molecules through hydrogen bonds with these hydroxyl functions can be readily achieved. 15-hydroxypentadecanoic acid and 16-hydroxyhexadecanoic acid have been dissolved in alcohols of different molecular lengths to explore solvent coadsorption in these systems further. STM images of solutions of 15-hydroxypentadecanoic acid in hexanol, heptanol, octanol, nonanol, decanol, and undecanol have been obtained and are described briefly in Table 1.

No solvent coadsorption is observed for 16-hydroxyhexadecanoic acid dissolved in alcohols. Instead, monolayers composed of only solvent are found when the solvent is decanol or undecanol. The particular structure of the tetramer formed by 16-hydroxyhexadecanoic acid when it self-assembles, where every −OH group is simultaneously bonded with two −COOH groups and one other −OH group (Figures 1d and 3c), excludes the introduction of monosubstituted alkanes such as alcohols into the same acid monolayer. Essentially, all possible −OH···HO− hydrogen-bonding sites on the 16-hydroxyhexadecanoic acid are occupied by self-association with other 16-hydroxyhexadecanoic acid molecules.

However, alcohol molecules can sometimes be integrated into the 15-hydroxypentadecanoic acid monolayers. Interestingly, only coadsorption with octanol has been observed so far (Table 1). The shortness of hexanol and heptanol appears to render them unstable on the surface (on the time scale of STM experiments) in this molecular mixture, though the coadsorption of heptanol in 5-[10-(2-methylbutoxy)-decyloxy]isophthalic acid

monolayers has been observed by De Feyter.[20] On the basis of its molecular length and the observed coadsorption with octanol, the longer nonanol would be expected to coadsorb with 15-hydroxypentadecanoic acid on the graphite surface. This, however, has not been observed to occur, possibly because of geometric considerations. As illustrated by the green arrows in Figure 2b, the space occupied by two octanol molecules (forming either a herringbone or collinear structure) almost equals the space occupied by one 15-hydroxypentadecanoic acid molecule. At the liquid−solid interface, molecules continuously undergo adsorption/desorption, where one solute molecule desorbs and can be replaced by solute or solvent molecules from solution. The assumption of such a dynamical process is in agreement with the observation that octanol molecules appear in various surface arrangements (aligned or forming herringbones) and permutations (from no solvent interspersed with the acid molecules to three double rows of coadsorbed species, from observations not shown here). The absence of coadsorption with nonanol is, therefore, likely due to the fact that two nonanol molecules do not fit into the space left empty by a desorbed 15-hydroxypentadecanoic acid molecule.

Alignment of Neighboring Molecular Axes in 16-Hydroxyhexadecanoic Acid. Recently, Fang and co-workers[15,26] noticed subtle differences in the alignment of physisorbed fatty acids' molecular axes in neighboring lamellae. In that study, the molecules 11-bromoundecanoic acid and 12-bromododecanoic acid self-assembled into patterns where the molecular axes in adjacent lamellae were offset from one another. A second organization pattern (exhibited by the molecule 2-bromohexadecanoic acid) is characterized by a surface structure where the molecular axes of molecules in adjacent lamellae are completely aligned. Furthermore, work by Hibino et al.[17] showed that unsubstituted fatty acids form a 2D surface structure where neighboring molecular axes are offset from one another, a feature identified through the position of the hydrogen-bonding carboxylic acid marker groups.

16-Hydroxyhexadecanoic acid dimers organize into a structure where neighboring molecular axes are aligned, as shown in the STM image in Figure 1c and by the superimposed black bars over two neighboring molecules in the model shown in Figure 3c. This is only the second observed example of this pattern (in addition to the SAM for physisorbed 2-bromohexadecanoic acid[26]). An organization of 16-hydroxyhexadecanoic acid where neighboring molecular axes are offset would prevent optimal hydrogen bonding between the carboxylic acid and alcohol groups, thereby compromising the stabilization of the monolayer by hydrogen bonding (Figure 3d).

A possible explanation[15] for the alignment or offset of molecular axes in neighboring lamellae is the differing orientations of the carboxylic acid functional group on the graphite surface, assuming that some degree of commensurability with the graphite surface is maintained. One orientation is characterized by an ~25° angle between the hydrogen bond direction and the long molecular axis. When molecular dimers are physisorbed onto graphite in this configuration, the molecular axes in neighboring lamellae will be offset. A second orientation is characterized by an ~45° angle between the hydrogen bond direction and the long molecular axis resulting in fatty acid dimers whose adjacent molecular axes are aligned. In fact, the 25° angle (offset) orientation for the fatty acid group is that depicted in Figure 3d, whereas the 45° angle (aligned) orientation is shown in Figure 3c. State-of-the-art molecular mechanics calculations in conjunction with high-resolution STM studies are currently underway to investigate further the source of the

alignment/offset between molecular axes in the surface self-assembly pattern of various fatty acid molecules.[27,28]

Conclusions

Monolayers formed by the disubstituted molecules 15-hydroxypentadecanoic acid or 16-hydroxyhexadecanoic acid physisorbed onto graphite have been successfully imaged by STM at the liquid−solid interface. Within one lamella, molecules of 15-hydroxypentadecanoic acid are always oriented parallel to one another while 16-hydroxyhexadecanoic acid molecules lie antiparallel to each other (interdigitate). The difference between these two molecular patterns can be explained by a new type of odd/even effect where different intermolecular hydrogen bonds are created or frustrated depending on the presence of an odd or even number of carbon atoms in the molecular chain. The surface arrangement of the 15-hydroxyhexadecanoic acid further allows for the coadsorption of alcohol solvent, though only the coadsorption of octanol has been observed because of geometric considerations that appear to be related to the fact that octanol molecules are just half the length of the 15-hydroxypentadecanoic acid molecules. The SAM composed of 16-hydroxyhexadecanoic acid also reveals that the molecular axes in adjacent lamellae are aligned, similar to the SAM formed by 2-bromohexadecanoic acid. These results contribute to a better understanding of the forces governing self-assembled monolayers and constitute important steps toward their design and manipulation.

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J. Phys. Chem. B, Vol. 107, No. 1, 2003 **179**

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