

Structures of alkanes and alkanols adsorbed on graphite in solution: Comparison with scanning-tunneling-microscopy images

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X-ray-diffraction studies have been performed on monolayers of long-chain alkanes and alkanols adsorbed from solution onto graphite. The data confirm the arrangements of these linear molecules on graphite reported in previous scanning-tunneling-microscopy (STM) studies and moreover refine the structures of the alkanol monolayers. The alkanol molecules form an incommensurate herringbone structure due to the formation of zigzag chains of hydrogen bonds, inconsistent with the conclusion of the STM studies.

I. INTRODUCTION

Adsorption of higher alkanes and alkanols from solution in a lower alkane onto graphite leads to the formation of close-packed monolayers of the molecules oriented with their carbon skeleton planes parallel to the surface.¹⁻⁴ *In situ* scanning-tunneling-microscopy (STM) studies have revealed that the monolayers possess a high degree of two-dimensional (2D) ordering; the structures of the adsorbed molecules have been deduced from analysis of their STM images.⁵⁻⁹ Although STM observations are now popular for a wide variety of molecular systems including amphiphilic molecules,^{10,11} liquid crystals,¹²⁻¹⁵ and biomolecules¹⁶⁻¹⁸ at the internal interface between two condensed media, there are many unsolved problems in STM imaging of molecules. The contrast mechanism is not well understood.^{5,12-15,18,19} Both the electric field from and mechanical forces due to the tip may have significant effects on adsorbed molecules.^{6,16,18,19} Moreover, it is known that a graphite substrate is particularly prone to imaging artifacts.^{16,17} *In situ* observations of these molecular systems by means of other methods with established principles are usually difficult because of the presence of air or liquid surrounding the molecules and therefore some uncertainty always remains in the structures deduced by STM.¹⁶⁻¹⁸ In this respect, diffraction studies of the same molecular monolayers investigated by STM is highly desirable. Very recently, Dai *et al.*²⁰ have performed both x-ray-diffraction and STM measurements of a liquid-crystal film adsorbed from gas phase onto signal-crystal graphite and have found a 10% discrepancy in the monolayer *d* spacing inferred by the two techniques.

In this work we report the x-ray-diffraction results of long-chain alkanes and alkanols adsorbed on graphite in solution. These are the simplest molecules among the organic adsorbates at the liquid-solid interface investigated by STM so far. The adsorbed structures of the molecules are simple compared to liquid-crystal molecules used more frequently in STM studies.^{12-15,20} Therefore, it may be expected that we are able to test independently the monolayer structures inferred from STM images by means of a conventional diffractometer. The results

confirm that the STM images of these simple molecules have reflected real arrangements of the molecules adsorbed on graphite. The structures deduced by the two different methods coincide in the case of the alkane monolayers but differ somewhat for those of the alkanols.

II. EXPERIMENT

In our experiments, the molecules were adsorbed from dilute solutions in *n*-heptane onto graphite, using a closed-circuit system. In this system the solution of a known concentration is circulated through an adsorption cell. The concentrations of the solutions were chosen so as to form the monolayers of close-packed molecules on graphite at 298 K.²⁻⁴ The substrate used was the recompressed exfoliated graphite, Grafoil.²¹ Grafoil sheets were equilibrated for 24 h at 298 K with the solutions in the cell fitted with Be windows, annealed in the solutions for 8 h at 308 K and then cooled to 298 K for x-ray-diffraction measurements. A stack of three Grafoil sheets was used and the cell was designed to minimize the thickness of solution through which the beam passed.²² The experimental apparatus of x-ray diffraction have been described in detail elsewhere.²¹ Cu $K\alpha$ radiation was used in the experiment. A diffraction pattern of the substrate in a pure solvent was also measured in order to obtain a background spectrum. All the diffraction patterns presented in this study are those with background subtracted. The resulting pattern contains broad profiles originating from the difference in diffuse scattering between pure solvent and solution. However, only sharp profiles due to the formation of the crystalline monolayers are considered in our analysis.

III. RESULTS AND DISCUSSION

A. Alkane monolayers

In Fig. 1, we show x-ray-diffraction patterns of docosane (C₂₂H₄₆) and dotriacontane (C₃₂H₆₆) monolayers adsorbed on graphite in solutions. Both patterns resemble each other and are surprisingly simple. Their simplicity suggests a high symmetry in the structures.

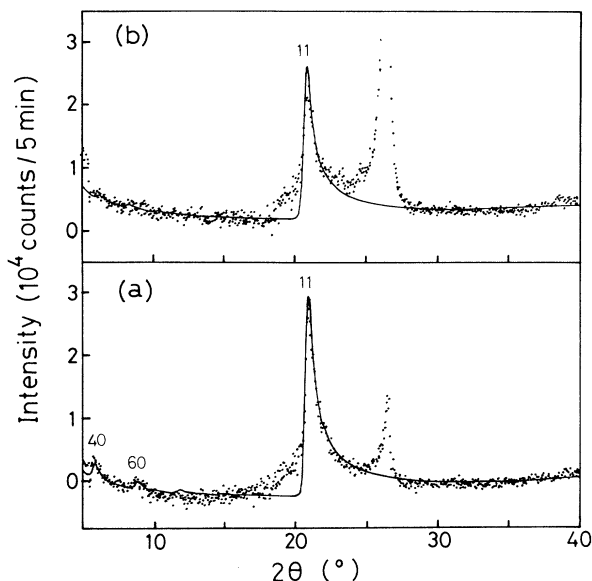


FIG. 1. X-ray-diffraction patterns of the alkane monolayers adsorbed from solution onto graphite: (a) docosane and (b) dotriacontane. Solid lines are fits to the data as described in the text.

There are two small peaks at lower angles and a strong peak near $2\theta=21.0^\circ$ for docosane, while there is only one peak at $2\theta=21.0^\circ$ for dotriacontane. An extra scattering around $2\theta=26^\circ$ comes from the combined effect of the incomplete subtraction of the strong (002) graphite reflection and the cross interference between the scattering from the adsorbed layer and from the graphite (002) plane.²³ Crystalline monolayers of butane and hexane, lower alkanes, physisorbed from gas phases onto graphite have a rectangular unit cell containing two molecules arranged in a herringbone pattern, commensurate with the substrate.^{24,25} However, this herringbone structure does not reproduce at all the observed diffraction patterns of both the monolayers.

The STM images of long-chain alkanes adsorbed from solutions onto graphite have exhibited highly ordered lamellae, the width of which nearly correspond to the length of the extended molecule.^{5-7,9} McGonigal, Bernhardt, and Thomson⁵ and Watel, Thibaudau, and Cousty⁹ have explained their STM images assuming the molecules of the parallel arrangement are commensurate with the graphite lattice and the carbon skeleton planes lie flat on the substrate. On the other hand, Rabe and Buchholz⁷ have considered that the molecules in the same arrangement are either commensurate or near commensurate with the substrate only in the direction along the lamellae and the carbon skeletons are oriented preferentially perpendicular to the graphite surface plane. Despite the distinct difference between them, both models produce similar diffraction patterns. Here, the diffraction pattern was calculated according to the powder-averaged Gaussian line shape²⁶ and the profile parameters were used as determined previously in this substrate.²¹ In addition, they closely resemble the observed diffraction patterns. This confirms the parallel ar-

range of the alkane molecules deduced from their STM images. The peak position of the (11) reflection is sensitive to the dimension of the short side of the unit cell and is almost independent of that of the long side. In the docosane monolayer we can determine the dimension of the long side from the peak position of the (40) and (60) reflections. The resulting lattice parameters are $a=60.0\pm 1.0 \text{ \AA}$ and $b=4.28\pm 0.02 \text{ \AA}$ for docosane and $b=4.28\pm 0.02 \text{ \AA}$ for dotriacontane. In the commensurate monolayer the dimension of b axis equals 4.26 \AA , namely, the separation between the second from the next carbon rows in graphite, while that of a axis amounts to 61.5 \AA for the docosane monolayer. Although our data seem to support the uniaxially incommensurate unit cells of the alkane monolayers proposed by Rabe and Buchholz,⁷ we are unable to distinguish between the two different molecular orientations proposed from interpretation of the STM images: the carbon skeleton planes parallel^{5,9} and perpendicular⁷ to the graphite surface. Figure 2 illustrates the structure of the monolayer docosane film formed on graphite in solution, due to the perpendicular-orientation model of the carbon skeletons.

B. Alkanol monolayers

We have measured the x-ray-diffraction patterns of nonanol ($C_9H_{19}OH$), decanol ($C_{10}H_{21}OH$), undecanol ($C_{11}H_{23}OH$), dodecanol ($C_{12}H_{25}OH$), and octadecanol ($C_{18}H_{37}OH$) adsorbed from solution onto graphite. An adsorption of nonanol shows only a very broad profile in the diffraction pattern, while adsorptions of the other alkanols result in crystalline patterns. They show two or three strong diffraction peaks in the 2θ range 18° – 22° , in addition to one weak peak at a lower angle. We limit ourselves here to the discussion of the decanol monolayer, because the following analysis indicates that this homologous series results in identical arrangements of the molecules on graphite. As Fig. 3 shows, the decanol monolayer exhibits only four peaks at $2\theta=10.0^\circ$, 18.6° , 20.0° , and 21.8° in the diffraction pattern. Figure 4 shows the concentration dependence of the x-ray-diffraction patterns for decanol adsorbed from solutions onto graphite. These concentrations cover the region of a step appearing in the adsorption isotherm of decanol from heptane solutions.² Although exact determination of coverage is impossible, the coverages range from a submonolayer to a nearly complete monolayer. When the concentration is increased, two diffraction peaks at $2\theta=18.6^\circ$ and 20.0° start to appear at a mole fraction of 15×10^{-3} and the peak positions do not change with further increasing concentration. The minimum concentration needed for formation of an ordered monolayer corresponds to just after the completion of the step in the ad-

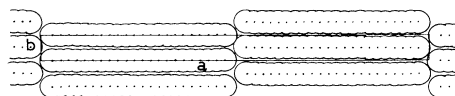


FIG. 2. Structure of the ordered monolayer of docosane adsorbed from solution onto graphite.

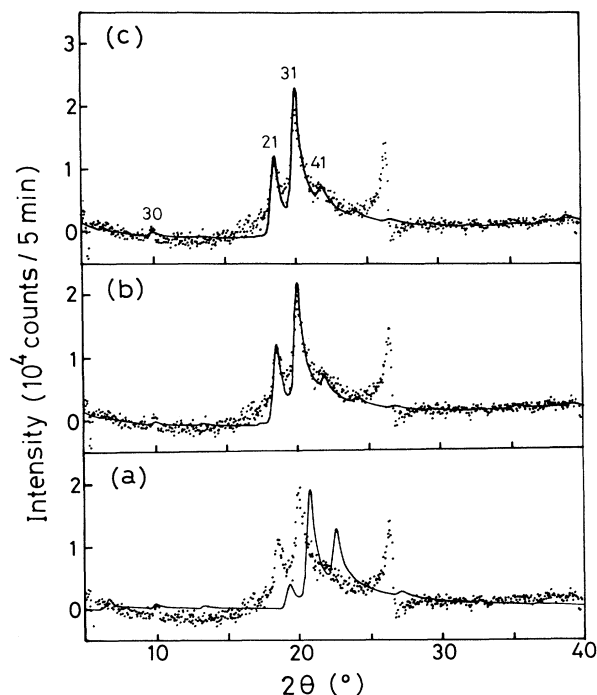


FIG. 3. Comparison of the observed diffraction pattern of decanol with the calculated diffraction patterns: (a) a partially commensurate herringbone model proposed from the STM studies, (b) an incommensurate herringbone model with the parallel orientation of the carbon skeletons against the graphite surface plane, and (c) an incommensurate herringbone model with the perpendicular orientation of the carbon skeletons.

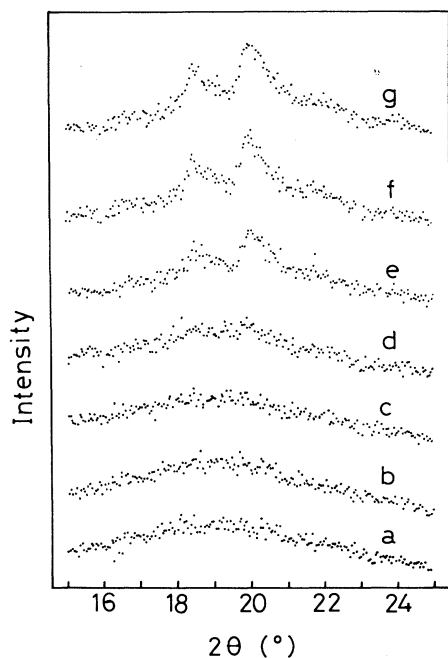


FIG. 4. X-ray-diffraction patterns of decanol adsorbed from solution onto graphite as a function of concentration at 298 K. Concentrations in mole fraction are as follows: (a) 5×10^{-3} , (b) 7×10^{-3} , (c) 9×10^{-3} , (d) 12×10^{-3} , (e) 15×10^{-3} , (f) 20×10^{-3} , and (g) 30×10^{-3} .

sorption isotherm,² namely, the formation of a nearly complete monolayer. This suggests that coadsorption of a small amount of the solvent molecules reduces greatly the long-range order in the decanol monolayer.

The STM images of long-chain alkanols on graphite have also exhibited highly ordered lamellae, although the patterns are different than those observed for the alkane monolayers.⁶⁻⁸ The images have been analyzed on the basis of formation of a herringbone structure in the monolayers.^{7,8} The molecules are assumed to be in the *trans* conformation with their carbon skeletal plane oriented perpendicular to the substrate by a steric effect. The monolayer is commensurate with the substrate only in the direction along the lamellae. As opposed to the case of the alkane monolayers, such a model proposed from the STM studies does not well reproduce the observed diffraction pattern [Fig. 3(a)]. Slight adjustment in the lattice parameters, however, results in a more improved fit between the observed and calculated patterns.

A crystalline monolayer of ethanol,^{27,28} a simple alkanol, physisorbed from a gas phase onto graphite has an incommensurate herringbone structure similar to the STM images observed for the long-chain alkanols adsorbed from solutions. Therefore, we tried to simulate the diffraction pattern further, assuming that the molecules are arranged in a herringbone pattern, incommensurate with the substrate. The incommensurate herringbone structure is concerned with the formation of zigzag chains of hydrogen bonds in the monolayer.^{27,28} The structure belongs to the plane group symmetry *pg* and there are two molecules in a rectangular unit cell. In these simulations, two conformations of the molecules, the perpendicular and parallel orientations of the carbon skeletons against the graphite surface plane, were considered. Averaged bond lengths and bond angles based on a single crystal structure of *n*-hexadecanol ($C_{16}H_{33}OH$) (Ref. 29) were assumed for the geometry of the molecule. The orientation and position of the molecule, as well as the lattice parameters, were varied within the limits of the plane-group symmetry with the assumption that the molecules are rigid and in the *trans* conformation. Only the C and O atoms were included in the calculation and identical thermal parameters of $B = 8 \text{ \AA}^2$ were incorporated. As a comparison of Fig. 3(b) with Fig. 3(c) shows, the perpendicular and parallel orientations of the carbon skeletons give indistinguishable diffraction patterns. And a fit between the observed and calculated diffraction patterns is reasonable for both the conformations. This indicates that an x-ray-diffraction pattern cannot discriminate between the parallel and perpendicular orientations of the carbon skeletons. The lattice and positional parameters determined from a comparison between the observed and calculated diffraction patterns are summarized in Table I, together with those for the monolayers of the other alkanols. Here, $xc1$ and $yc1$ denote the coordinates of the C atoms in the terminal position of the molecules and θ the orientation angles of the alkyl chain against the *a* axis. All these parameters determined here give a reasonable packing of each molecule on the substrate. For the monolayers of undecanol, dodecanol, and octadecanol $xc1$ was fixed at 1.4 \AA in the

TABLE I. Structural parameters of alkanols adsorbed on graphite in solution.

	a (Å)	b (Å)	$xc1$ (Å)	$yc1$ (Å)	(deg)
Decanol	26.5 ± 0.3	5.17 ± 0.02	1.2 ± 0.2	0	26.8 ± 0.3
Undecanol	29.5 ± 0.3	5.01 ± 0.02	1.4	0	25.2 ± 0.3
Dodecanol	32.0 ± 0.4	5.04 ± 0.02	1.4	0	24.6 ± 0.8
Octadecanol	45.1 ± 0.5	5.04 ± 0.02	1.4	0	26.5 ± 0.3

simulations of the diffraction patterns, because it gives a physically reasonable contact between the neighboring molecules. The structure of the monolayer decanol film formed on graphite in solution, due to the perpendicular-orientation model of the carbon skeletons, is illustrated in Fig. 5.

In the partially commensurate structure of the alkanol monolayers proposed from the STM studies,^{7,8} the dimension of the b axis and the orientation angle of the alkyl chain become 4.92 \AA and 30° , respectively. For all the alkanol monolayers we investigated the dimensions of the b axis and the orientation angle are $\sim 5.1 \text{ \AA}$ and $\sim 26^\circ$, respectively. Therefore, it is evident that the monolayers of long-chain alkanols are incommensurate with the graphite surface even in the direction along the lamellae, inconsistent with the conclusion of the STM studies.^{7,8} The larger lattice parameters obtained by x-ray diffraction do not seem to arise from differences in experimental conditions related to the coverage or the use of a solvent. Our experiments were done near monolayer completion and our results for the alkane monolayers are in good agreement with the STM values. Also, the STM studies⁷ show that the structures of the alkane and alkanol monolayers are independent of the kind of the solvents used. As graphite is hydrophobic and hydrogen bonding is more directional and relatively strong compared with the other intermolecular forces, monolayers of hydrogen-bonding molecules on graphite usually take incommensurate structures controlled mainly by adsorbate-adsorbate interactions.^{28,30-33} In the STM studies the conclusion concerning the incommensurability between adsorbate and substrate comes from an observation of a regular modulation of the contrast in STM images.^{7,34} Such a modulation has been thought to arise from a Moiré pattern between the lattices of the graphite and of the monolayer. The parallel separations of the alkanol molecules are estimated to be $4.5\text{--}4.6 \text{ \AA}$ from their structural parameters, while the corresponding separation between the second from the next carbon rows in graphite is 4.26 \AA . This mismatch is expected to lead to

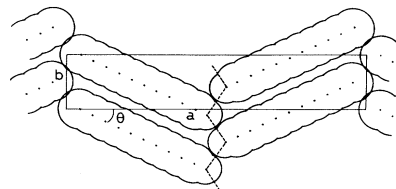


FIG. 5. Structure of the ordered monolayer of decanol adsorbed from solution onto graphite.

an observation of a distinct superstructure along the lamellae when the molecular axes are oriented parallel to a carbon chain in graphite. Therefore, the lack of discernible superstructure along the lamellae in the STM images of the alkanol monolayers^{7,8} might indicate tilting of the molecular axes relative to the graphite axis.

IV. CONCLUSION

We have studied the structures of the long-chain alkane and alkanol monolayers adsorbed on graphite in solution using x-ray diffraction. The diffraction data confirm the arrangements of these molecules on graphite deduced from their STM images and moreover refine the structures of the alkanol monolayers. The alkane molecules assumed to be in the *trans* conformation are aligned parallel to each other and are either commensurate or near commensurate with the substrate only in the direction along the lamellae. The alkanol molecules, which form a herringbone structure, are incommensurate with the substrate even in the direction along the lamellae, inconsistent with the conclusion of the STM studies.^{7,8} This indicates that the absence of a Moiré pattern in STM images is not a reliable indicator of commensurability. As the arrangements of the adsorbed molecules and the monolayer lattice parameters obtained by the two techniques nearly coincide with each other, the effects due to the tip and imaging artifacts are thought to be avoided or insignificant in careful STM experiments. The contrast mechanism has often been discussed on the basis of the superposition of assumed molecular models with observed images.^{5,12-14} However, uncertainty in the monolayer structures may easily lead to incorrect conclusions regarding contrast mechanisms. It is hoped that the improved accuracy in the determination of the monolayer lattice parameters and molecular orientations obtained in this work will lead to a better understanding of the contrast mechanisms in STM of organic monolayers.

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