X-ray Study of Alkanediols on Graphite

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X-ray diffraction measurement have been performed on the monolayers of alkanediols ($HO(CH_2)_nOH$, $n =$ 9, 10, 11, 12) adsorbed from vapor onto graphite. The results clealy show that the monolayers of the diols take two states of a metastable and a stable phase depending upon their annealing temperatures. All of the metastable monolayers take herringbone structure, regardless of the kind of diols. On the other hand, the stable monolayers take different molecular arrangements depending upon either an odd number of carbon atoms or an even number of carbon atoms. The two types of packing observed in the stable monolayers are closely related to the different conformations of the hydroxyl headgroups, and the phase transition of the metastable to stable monolayers accompany the conformational change of the headgroups for odd diols.

1. Introduction

Monolayer films of simple molecules adsorbed on the basal plane of graphite show a wide variety of phases that occur in a delicate balance between molecule–molecule and surface–molecule interactions.[1,2] Some of these surface phases resemble three-dimensional (3D) gases, liquids, or solids, but some of them have no analogues in bulk matter. The careful study of these phases and phase transitions gives not only much valuable information about the forces involved in physisorption but also a better understanding of intermolecular potentials and molecular behavior in three dimensions. In recent years we have carried out X-ray diffraction measurements on the alkanols,[3–9] in order to elucidate the role of hydrogen bonds and molecular shape in determining the structures and melting behavior of adsorbed layers. Hydrogen bonds are directed interactions whose energies lie between those of covalent bonds and nonspecific, intermolecular interactions.[10] All the data we have obtained so far clearly show that the monolayer structures are mainly determined by hydrogen bonds between hydroxyl groups, and unusual melting behavior is observed for the monolayers of linear-chain alkanols with alkyl chains containing more than three carbon atoms.[7,9]

Alkanediols have hydroxyl groups at both molecular ends. Bulk crystals of nonanediol and decanediol take different packing structures, which are closely related to their different conformations of the hydroxyl headgroups.[11] Recent scanning-tunneling-microscopy (STM) observations of alkanediols adsorbed from solutions onto graphite have shown a similar odd–even effect of carbon number on their two-dimensional (2D) molecular packings.[12] This suggests that the monolayers of alkanediols become good systems for exploring the delicate balance between the packing properties of hydrocarbon chains and the conformational properties of hydroxyl headgroups in 2D crystals on solid surfaces. In addition, diffraction studies of the same molecular monolayers investigated by STM are highly desirable, because there are many unsolved problems in STM imaging of molecules,[13] such as the contrast mechanism, the electric field effect from and/or mechanical forces due to the tip, and the imaging artifacts of a graphite substrate. In this paper we report the results of our intensive X-ray diffraction studies on the monolayers of alkanediols ($HO(CH_2)_nOH$, $n =$ 9, 10, 11, 12) adsorbed from vapor onto graphite. The monolayers of the diols formed on graphite in gas adsorption take two states of a metastable and a stable phase depending upon their annealing temperatures. The STM images observed in solutions have reflected real arrangements of the molecules in their stable phases. Two types of packing observed in the stable 2D crystals of alkanediols are closely related to the different conformations of the hydroxyl headgroups and the phase transition of the metastable to stable monolayers accompany the conformational change of the headgroups for diols with an odd number of carbons.

2. Experimental Section

Alkanediols ($HO(CH_2)_nOH$, $n =$ 9, 10, 11, 12) were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. The substrate used was the recompressed exfoliated graphite, Grafoil. Prior to adsorption, all the substrates were evacuated for 5 h at 623 K. Grafoil sheets (0.5 g) and a small amount of diols (4–10 mg) in a Pyrex tube were evacuated for 1 h at room temperature, sealed by glass-blowing and then heated for 12 h at a particular temperature between 353 and 403 K where the vapor pressures of the diols become significant. After the ample containing diols and graphite was heated, however, a part of the loaded diols always remained in the ample without being transferred onto graphite. The Grafoil sheets were transferred into a diffraction cell fitted with a Mylar window and evacuated at progressively higher temperatures until most of the diol molecules were removed from the surface. The evacuation temperature was raised at ca. 10 K intervals. The Grafoil was resistively heated in vacuo for 2 h at each temperature. At each stage of evacuation, the substrate was cooled to room temperature and the X-ray diffraction pattern was measured. A background spectrum of the Grafoil was obtained at a final stage of evacuation. All the diffraction patterns presented in this study are those with the Grafoil background subtracted. The surface area of the substrate was determined from the adsorbed amount at the commensurate–incommensurate transition of Kr by assuming the cross section of Kr to be 0.1572 nm^2.[14]

X-ray diffraction patterns were performed on a two-circle diffractometer (Rigaku, Rint 2500) equipped with a peltier

TABLE 1: Loading Amount of Diols (HO(CH$_2$)$_n$OH) against 0.5 g of Graphite and Adsorption Temperatures

n	loading amount (mg)	adsorption temperature (K)
9	4.5	353
	6.0	353
		363
		393
	10.0	353
10	6.0	353
		363
		373
11	6.0	363
		373
		383
		393
12	6.0	373
		383
		393

cooled silicon detector (Kevex) and a rotating-anode source, operated at 12 kW. The measurements were carried out with Cu Kα radiation in the symmetrical transmission geometry.

3. Results

The effects of adsorption temperature, evacuation temperature and amount of the diols on the diffraction patterns were explored. Table 1 summarizes these experimental conditions. When the loaded diols are all adsorbed on the graphite surface, the surface coverages of nonanediol, decanediol, undecanediol, and dodecanediol correspond to 1.6−4.0, 2.2, 2.0, and 1.9 molecule/nm^2, respectively. The patterns always showed sharp peaks of saw-tooth shape,[15] typical of a crystalline monolayer. The diffraction patterns of the monolayers formed at lower temperatures changed in shape upon subsequent evacuation at elevated temperatures. The resulting patterns were the same as those of the monolayers formed by adsorption at higher temperatures. Therefore, it is evident that the monolayers of the diols formed on graphite in gas adsorption take the two states of the metastable and stable monolayers depending upon their annealing temperatures. The diffraction patterns and their changes upon annealing at elevated temperatures may be divided into two groups, namely, those of the diols with an odd number of carbons and those with an even number of carbons.

3.1. Nonanediol and Undecanediol. As Figure 1 shows, the X-ray diffraction pattern of nonanediol measured at room temperature changes with adsorption temperature. At the adsorption temperature of 353 K, the diffraction pattern shows a sharp peak at $2\theta = 21.0°$ together with two-shoulder peaks at $2\theta = 19.9$ and $22.2°$. This pattern often shows an additional small peak at $2\theta = 7.2°$. When the adsorption temperature was raised to 393 K, the diffraction pattern obtained shows only one peak at $2\theta = 19.7°$. At 363 K, overlapping of these two diffraction patterns is observed. When the monolayers of nonanediol adsorbed at 353 and 363 K were subsequently evacuated near 393 K, a small amount of the diol was desorbed from the surface and the diffraction pattern always changed to that of nonanediol adsorbed at 393 K. Such a change in diffraction pattern was independent of the amount of nonanediol initially loaded. All these results clearly indicate the presence of the metastable and stable monolayers of nonanediol on graphite.

The STM images of the diols adsorbed from solution onto graphite have exhibited two different types of highly ordered lamellae depending upon either an odd number of carbon atoms
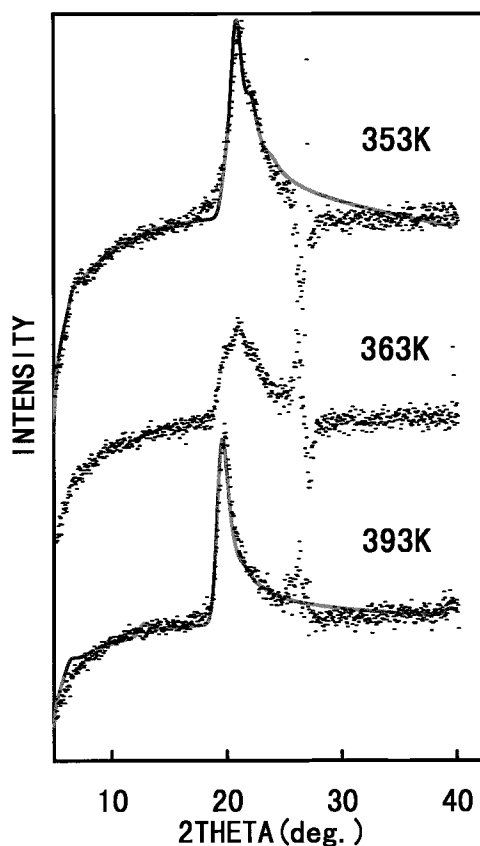

Figure 1. X-ray diffraction patterns of nonanediol adsorbed on graphite at a loading amount of 6 mg and at various temperatures. Solid lines are fits to the data as described in the text.

or an even number of carbon atoms.[12] Even diols form a herringbone structure. Odd diols take parallel arrangement of the molecules where the molecular long axes are oriented 90° with respect to the lamella axes. Similar odd−even effects have been observed for the bulk structure of nonanediol and decanediol.[11] Two types of packing observed in the bulk crystals arise from different conformations of the molecules. The molecules of decanediol adopt an all-trans conformation while those of nonanediol adopt a C$_\alpha$−OH gauche conformation about the C$_\alpha$−C$_\beta$ bond at one end.

Simulation of X-ray diffraction patterns shows that the observed pattern of the stable monolayer of nonanediol is well-reproduced by the parallel arrangement of the molecules deduced by the STM images. The structure belongs to the plane group symmetry pg, and there are two molecules in a rectangular unit cell. Averaged bond lengths and bond angles based on single-crystal structures[11] of nonanediol and decanediol were assumed for the geometry of the molecules. The position of the molecules and the lattice parameters were varied within the limits of plane group symmetry with the assumption that the molecules of a gauche conformation at one end lie flat on the surface. Parallel orientation of the carbon skeletons against the graphite surface plane was also assumed, because an X-ray diffraction pattern cannot discriminate between the parallel and perpendicular orientations of the carbon skeletons against the surface.[6] Only the C and O atoms were included in the calculation and identical thermal parameters of $B = 6$ Å^2 were incorporated. The diffraction pattern was calculated according to the powder-averaged Gaussian line shape[15] appropriate to a crystalline monolayer, and the profile parameters were used as determined previously in this substrate.[16] The calculated pattern is shown as a solid line in Figure 1. The quality of the fit is

X-ray Study of Alkanediols on Graphite

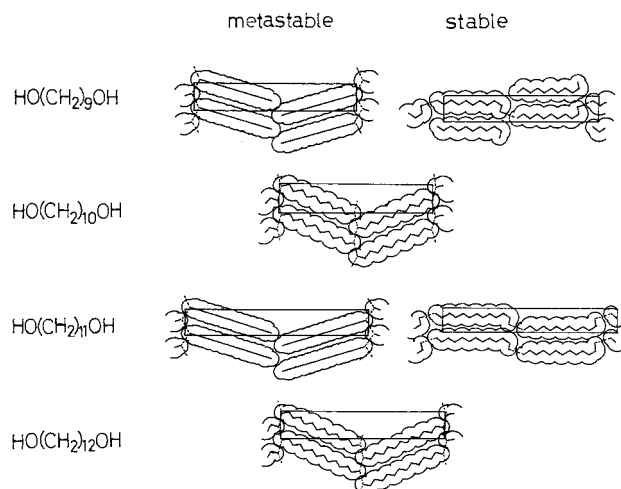*J. Phys. Chem. B, Vol. 102, No. 28, 1998* **5497**

Figure 2. Structures of the stable and metastable monolayers of alkanediols on graphite.

reasonable, except for a small region around $2\theta = 26.6°$. This feature comes from the incomplete subtraction of the strong (002) graphite reflection. The molecular structure of an all-trans conformation gave an extra shoulder peak around $2\theta = 21.2°$. The structure is illustrated in Figure 2. In a final stage of refinement, the OH groups of a gauche conformation were slightly lifted from the surface in order to avoid the collision of the OH groups with the CH_2 groups of the neighboring molecules. The molecules of a gauche conformation at one end are arranged in rows with their long axes normal to the row in the monolayer. Inter-row hydrogen bonds are formed between molecules of unlike end-of-chain gauche and trans C−OH conformations. Similar arrangement of the molecules of a gauche conformation at one end is observed on the (100) plane of the bulk crystal of nonanediol.[11]

Parallel arrangement of the molecules did not well reproduce the observed diffraction pattern of the metastable monolayer of nonanediol. In searching for other molecular arrangements, we found out that the herringbone arrangement of the molecules of an all-trans conformation was appropriate to the metastable monolayer of nonanediol. The orientation and position of the molecules, as well as the lattice parameters, were varied within the limits of plane group symmetry pg with the assumption that the molecules of an all-trans conformation lie with the perpendicular orientation of the carbon skeleton against the surface. Here, the perpendicular model was taken from a consideration about the parallel separation of the molecules in the metastable monolayers of odd diols, as will be described later. The calculated pattern is also shown as a solid line in Figure 1. The quality of the fit is reasonable, except for a shoulder peak around $2\theta = 19.9°$ and the incompleted subtraction of the graphite (002) reflection. The former presumably comes from the presence of the stable phase. The herringbone structure of the metastable phase is also illustrated in Figure 2. The structure resembles that of the crystalline monolayer of *n*-propanol adsorbed on graphite.[7] The molecules are interlinked at one end by inter-row O−H···O hydrogen bonds. The hydroxyl groups at the opposite ends of the molecules do not form hydrogen bonds. Figure 3 shows the X-ray diffraction patterns of the metastable and stable monolayers of undecanediol. Similarly, the herringbone and parallel arrangement of the molecules can reproduce well the diffraction patterns of the metastable and stable phases, respectively. The lattice and positional parameters determined from a comparison between the observed and calculated diffraction patterns are summarized in Table 2,
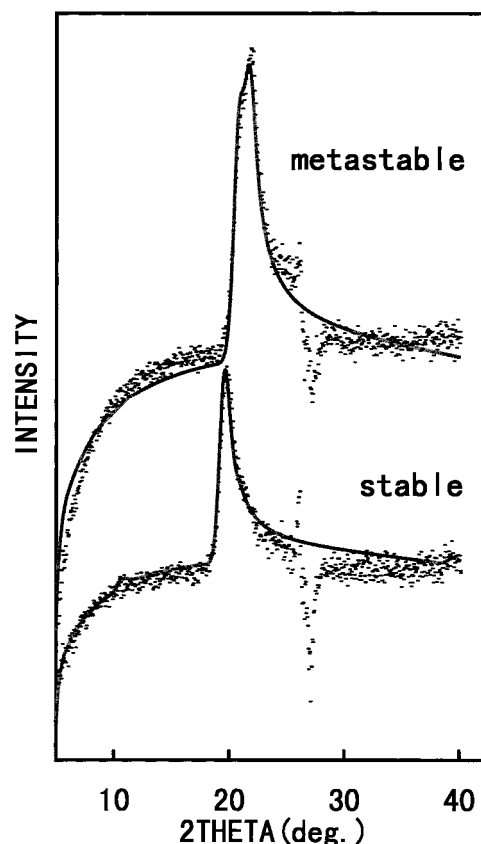

Figure 3. X-ray diffraction patterns of the metastable and stable phases of undecanediol on graphite. The metastable monolayer was obtained by adsorption of undecanediol with a loading amount of 6 mg and at 383 K. The stable monolayer was obtained by a subsequent evacuation of the metastable phase at 403 K. Solid lines are fits to the data as described in the text.

TABLE 2: Structural Parameters of Alkanediols (HO(CH$_2$)$_n$OH) Adsorbed on Graphite

	n	a (Å)	b (Å)	$xc1$ (Å)	$yc1$ (Å)	θ (deg)
stable phases	9	4.62	28.0	2.02	0	0
	10	27.2	5.16	1.76	0	23.6
	11	4.61	33.3	2.02	0	0
	12	31.7	5.18	1.77	0	24.5
metastable phases	9	26.6	4.54	1.95	0	16.0
	10	27.8	5.08	1.76	0	23.6
	11	31.9	4.47	2.00	0	16.5
	12	33.0	5.05	1.82	0	23.5

together with those for the monolayers of decanediol and dodecanediol described in a subsequent section. Here, $xc1$ and $yc1$ denote the coordinates of the C atoms in a trans C−OH conformation and θ denotes the orientation angles of the alkyl chain against the long axis of the unit cell.

3.2. Decanediol and Dodecanediol. As Figure 4 shows, the X-ray diffraction pattern of decanediol adsorbed at 363 K shows two peaks at $2\theta = 18.8$ and $20.1°$. When this sample was then evacuated at 383 K, only a slight lowering of the peak positions was observed. A herringbone arrangement of the molecules deduced from the STM images[12] results in a reasonable fit between the observed and calculated patterns for both metastable and stable monolayers of decanediol on graphite. The orientation and position of the molecules, as well as the lattice parameters, were varied within the limits of plane group symmetry with the assumption that the molecules of an all-trans conformation are arranged in a herringbone pattern. The structure belongs to the plane group pg. The structure of the
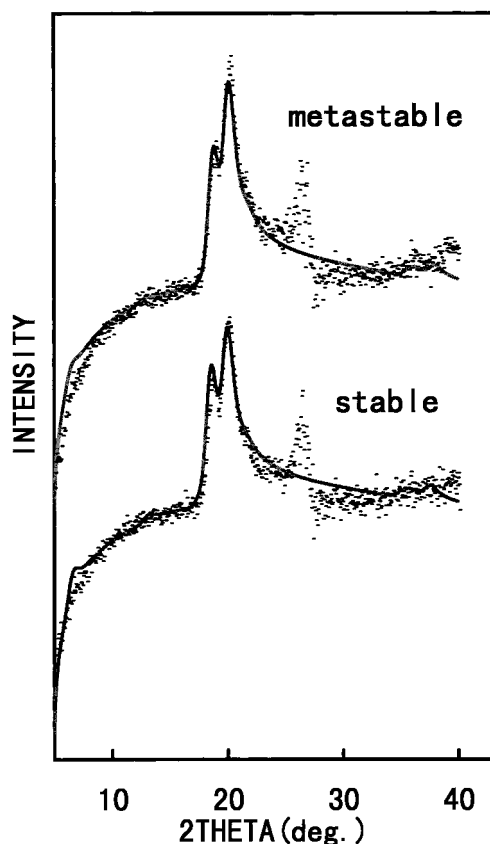
Figure 4. X-ray diffraction patterns of the metastable and stable phases of decanediol on graphite. The metastable monolayer was obtained by adsorption of decanediol with a loading amount of 6 mg and at 363 K. The stable phase was obtained by a subsequent evacuation of the metastable phase at 383 K. Solid lines are fits to the data as described in the text.

Figure 5. X-ray diffraction patterns of the metastable and stable phases of dodecanediol on graphite. The metastable monolayer was obtained by adsorption of dodecanediol with a loading amount of 6 mg and at 393 K. The stable phase was obtained by a subsequent evacuation of the metastable phase at 413 K. Solid lines are fits to the data as described in the text.

stable phase of decanediol on graphite is illustrated in Figure 2. The molecules are interlinked at both ends by hydrogen bonds. Similar herringbone arrangement of the molecules is found on the (100) plane of the bulk crystal of decanediol.[11] Figure 5 shows the X-ray diffraction patterns of the metastable and stable monolayers of dodecanediol as well. Similarly, a herringbone model gives a reasonable fit between the observed and calculated patterns for both the phases. The lattice and positional parameters determined are also summarized in Table 2. Here, xc1 and yc1 denote the coordinates of the C atoms adjacent to the OH groups in the terminal position of the molecules. All the monolayers of even and odd diols are incommensurate with the substrate.

4. Discussion

The 2D packings of long-chain molecules are dependent upon the kinds of functional group at a molecular end.[17] This reveals a significant role of hydrogen bonds at molecular ends on their 2D packings. The hydrogen bonds between the OH groups tend to be formed along the direction of the sp^3 orbitals of the oxygen atoms,[11,18,19] even in the monolayers of short-chain alkanols adsorbed on graphite.[3] The herringbone arrangement in the metastable monolayers of odd diols does not fulfill this requirement for intermolecular hydrogen bonds at one ends. On the other hand, hydrogen bonding between molecules of unlike end-of-chain gauche and trans C—OH conformations is effectively formed in the stable monolayers of odd diols. The structural parameters indicate that the parallel separations of the molecules in the metastable and stable monolayers of odd
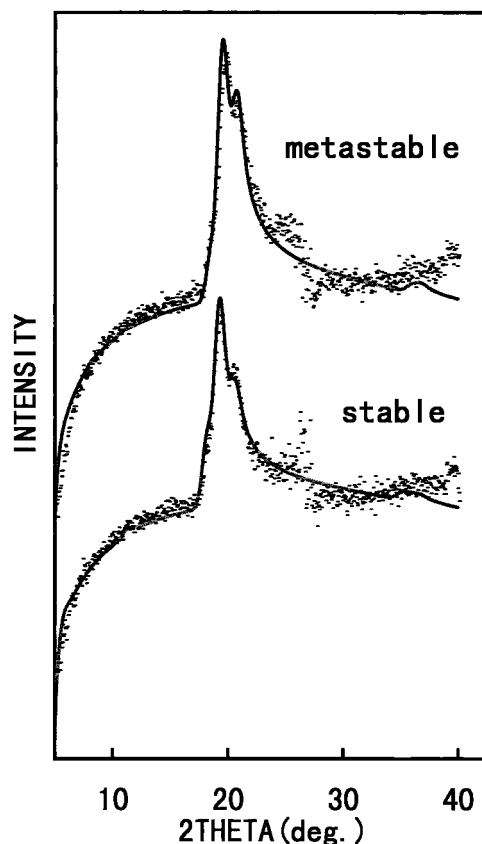
diols are ~4.3 and ~4.6 Å, respectively. In the metastable monolayers of odd diols, the carbon skeletons must be oriented preferentially perpendicular to the graphite surface plane because of their short separations with neighbors, while in the stable phases the carbon skeleton planes would lie flat on the substrate. This suggests that the packing properties of the hydrocarbon chains prevail in the metastable monolayers while both the surface—molecule interaction and the intermolecular hydrogen bonds at both ends are optimized in the stable monolayers. In even diols, the herringbone arrangement of the molecules of an all-trans conformation is well-compatible with effective intermolecular hydrogen bonds at both ends. The parallel separations of the molecules increase slightly with the phase transition of the metastable to stable monolayer. Therefore, the surface—molecule interaction also prevails in the stable phase of even diols.

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X-ray Study of Alkanediols on Graphite

J. Phys. Chem. B, Vol. 102, No. 28, 1998 **5499**

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