

Solvent Effects on the Monolayer Structure of Long n -Alkane Molecules Adsorbed on Graphite

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Neutron diffraction patterns of dotriacontane (n -C₃₂D₆₆) monolayers adsorbed on an exfoliated graphite substrate from a heptane (n -C₇D₁₆) solution reveal striking differences in the molecular orientation, lattice constant, and coherence length from those of the same monolayer adsorbed from the gas phase. Neither n -C₃₂D₆₆ monolayer phase appears to be fully consistent with Groszek's model of n -alkane registry on the graphite (0001) surface. A reversible transformation between the two monolayer phases can be induced by adding as little as a monolayer of the heptane solvent.

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The phenomenon of selective adsorption in which one molecular species preferentially adsorbs from solution at a solid interface is of fundamental interest in polymer science and plays an essential role in technologically important processes such as adhesion, lubrication, and coatings [1–3]. It has long been recognized that prototypical systems for such studies are binary solutions of n -alkane molecules [CH₃(CH₂) _{n} CH₃] exposed to a graphite substrate in which the longer solute molecule adsorbs at the expense of the shorter solvent molecule.

Thermodynamic experiments investigating the selective adsorption of n -alkanes on graphite began over 40 years ago. Over a decade passed before a specific mechanism was offered for selective adsorption in these systems. From his detailed adsorption isotherm measurements on n -C₃₂H₆₆/ n -C₇H₁₆ solutions, Groszek [4] inferred that the n -C₃₂D₆₆ (n -dotriacontane) molecule occupied an area on the graphite basal-plane surface corresponding to a density $\sim 10\%$ greater than that estimated from its bulk crystal structure. To explain this compression and the preferential adsorption of the longer molecule, Groszek proposed a simple model of molecular registry illustrated in Fig. 1(a). In its lowest-energy (*trans*) configuration, the planar zigzag carbon skeleton of an n -alkane molecule can be aligned parallel to the graphite surface such that each H atom closest to the surface nearly occupies the center of a graphite carbon hexagon. Because the methyl endgroups occupy a larger surface area than the methylene groups, Groszek suggested that longer n -alkane molecules could form more H-atom "contacts" per unit area than shorter ones and hence preferentially adsorb.

In subsequent adsorption isotherm experiments, Findenegg and co-workers [5,6] found the isotherms of long n -alkane molecules adsorbed from a short n -alkane solution to be "S shaped" in the submonolayer regime rather than of the Langmuir type expected when adsorbate-substrate interactions dominate. They concluded that the strong preferential adsorption of the long-chain n -alkanes is caused mainly by lateral interactions within the adsorbed layer and suggested that close-packed ordered arrays of the long n -alkane molecules formed at the solid interface.

More recently, scanning tunneling microscopy (STM) studies have confirmed the long-range order anticipated [5,6] for long-alkane monolayers on graphite basal-plane surfaces. McGonigal, Bernhardt, and Thomson [7] interpreted their images of n -C₃₂H₆₆ monolayers in terms of

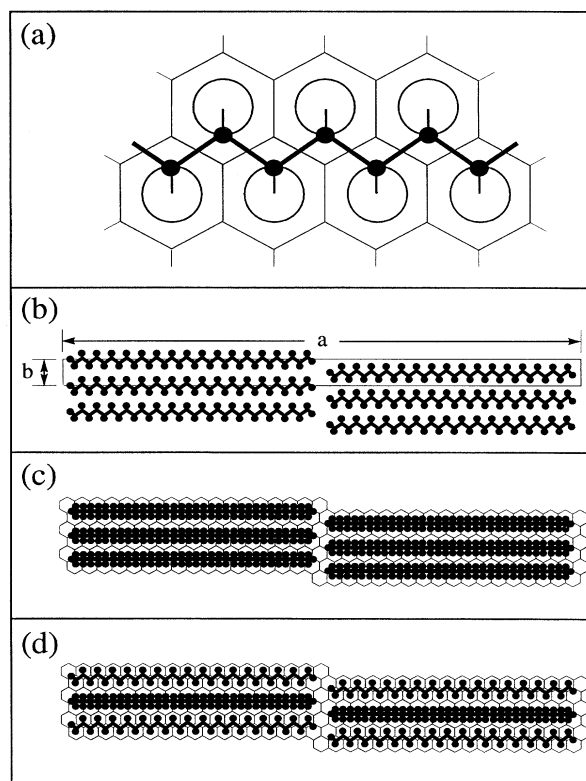


FIG. 1. (a) Schematic representation of Groszek's model (Ref. [4]) showing molecular registry of n -alkanes on a graphite basal-plane surface; (b) proposed unit cell of the vapor-deposited n -C₃₂D₆₆ monolayer; (c) unit cell of a n -C₃₂D₆₆ monolayer in which the carbon skeletal plane is perpendicular to the graphite surface; (d) proposed unit cell of the solution-deposited n -C₃₂D₆₆ monolayer in which the molecules have alternating parallel and perpendicular orientations within a lamella.

Grozek's model of molecular registry on the graphite surface. The molecules were observed to pack in rows or lamellae of width equal to the length of the molecule in its *trans* configuration with an intermolecular spacing within each lamella of 4.26 Å, the minimum separation consistent with Grozek's model. A similar interpretation has been made in more recent STM experiments on other long *n*-alkane monolayers [8].

In contrast, Rabe and Buchholz have argued [9,10] that the intermolecular spacing of 4.26 Å inferred from their STM images of long *n*-alkane monolayers is too small for the molecules to be oriented with the plane of their carbon skeleton parallel to the graphite surface. Noting that in solid bulk *n*-alkanes the intermolecular spacing is 4.2 and 4.8 Å in directions perpendicular and parallel to the molecular carbon planes, respectively [11], they proposed that the long *n*-alkane skeletal plane is perpendicular to the graphite surface. A recent x-ray scattering experiment has verified the 4.26 Å intermolecular spacing [12] but was unable to determine the molecular orientation.

Thus the validity of Groszek's model is yet to be established. Furthermore, in no experiment to date has the structure of the long-alkane monolayer been studied in the absence of the short-alkane solvent, i.e., as deposited from its vapor phase. The effect of the solvent on the long-alkane monolayer structure is then unknown, further hindering a microscopic understanding of the selective adsorption process.

In this paper, we report neutron diffraction experiments which allow us to compare the monolayer structure of a long-alkane molecule, *n*-dotriacontane (*n*-C₃₂D₆₆), adsorbed on a graphite basal-plane surface from its vapor phase with that of the monolayer selectively adsorbed from a solution of *n*-heptane (*n*-C₇D₁₆). The neutron diffraction patterns were obtained using the two-axis diffractometer equipped with a five-counter multidetector data-acquisition system [13] located at C-port of the Missouri University Research Reactor. The measurements were performed in a transmission geometry, as in previous experiments [14,15], but utilized a longer wavelength of 4.35 Å appropriate to the large monolayer unit cell of the long-alkane molecules. The sample preparation techniques have been described in detail elsewhere [16]. Briefly, the substrates were recompressed exfoliated graphite (Grafoil) [17], whose surface area was calibrated from a nitrogen vapor pressure adsorption isotherm at 77 K [18]. The *n*-C₃₂D₆₆ adsorbate and the *n*-C₇D₁₆ solvent (hereafter referred to as C32 and C7, respectively) were 98% deuterated and used as supplied [19]. Vapor deposition of the C32 monolayer was accomplished by heating in a stainless steel sample cell at 280 °C for 48 h. The monolayer adsorbed from the C7 solution was prepared by Soxhlet extraction within a quartz sample cell. In both cases, background diffraction patterns were measured at room temperature before adsorption of the C32.

The room-temperature diffraction pattern of the vapor-deposited C32 monolayer is shown in Fig. 2(a). Use of the longer wavelength neutrons and deuteration of the monolayer yields better contrast with the substrate than obtained in x-ray diffraction experiments [12]. In particular, the (*h*0) series of Bragg peaks can now be discerned and yield a value $a = 87 \pm 1.5$ Å for the long dimension of the unit cell [Fig. 1(b)].

However, the most striking feature of the diffraction pattern in Fig. 2(a) is the position of the (11) Bragg peak which corresponds to a lattice constant $b = 4.64$ Å. This value is 9% larger than that inferred in STM experiments [7,9,10] for monolayers deposited from solution and is compressed ~3% from the intermolecular separation of 4.8 Å found in bulk crystals parallel to the carbon planes [11]. The larger value of b suggests that the C32 molecules adsorb from the vapor phase with their carbon skeletal planes *parallel* to the graphite (0001) surfaces as found previously for the shorter *n*-alkanes [14,15]. Consistent with this interpretation, the diffraction profile calculated for the parallel orientation gives a better fit to the ob-

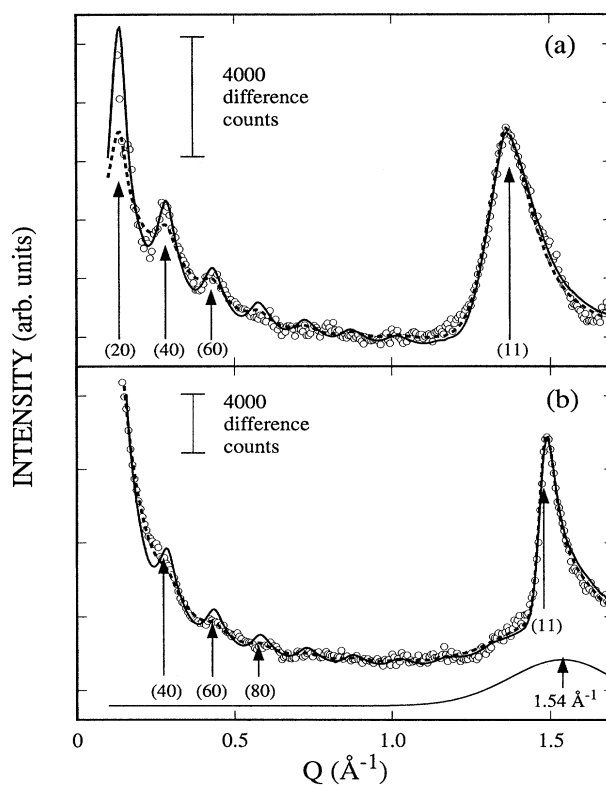


FIG. 2. Neutron diffraction patterns of *n*-C₃₂D₆₆ monolayers on graphite after background subtraction: (a) vapor deposited and (b) solution deposited. In both cases, the solid line is the calculated profile for the parallel model in Fig. 1(b) and the dashed line is that for the perpendicular model in Fig. 1(c). A Gaussian component centered at $Q = 1.54$ Å⁻¹ has been added to the pattern in (b) to represent the scattering from the C32/C7 solution.

served Bragg peak intensities as shown by the solid curve in Fig. 2(a) [20]. Assuming a perpendicular orientation of the C32 carbon skeletal plane (dashed curve) yields too little intensity for the low- Q ($h0$) series of peaks. Also, a parallel molecular orientation is consistent with potential energy calculations on C32 monolayer clusters (see Ref. [15]) in which the value of the b lattice constant is fixed at the experimentally measured value of 4.64 Å.

Also noteworthy in the diffraction pattern of the vapor-deposited C32 monolayer in Fig. 2(a) is the width of the (11) Bragg peak which corresponds to a coherence length $L = 38$ Å (about eight molecules wide) along the \mathbf{b} direction [see Fig. 1(b)]. This value of L is considerably less than the ~ 120 Å obtained for monolayers of shorter alkanes on the same substrate [14,15] and for the C32 monolayer deposited from solution as described below. To investigate whether the shorter coherence length resulted from a metastable phase, we annealed the vapor-deposited sample for extended periods at temperatures up to 320 °C but found no increase in L .

It is interesting to compare the room-temperature diffraction pattern of the vapor-deposited C32 monolayer [Fig. 2(a)] with that of a monolayer deposited from a C32/C7 solution [Fig. 2(b)]. Although the substrate was completely immersed in the solution during sample preparation, the diffraction pattern was obtained with a smaller amount of C7 present, equivalent to ~ 9 layers, in order to better resolve the scattering from the C32 monolayer. In contrast to the vapor-deposited C32 monolayer but in agreement with previous STM [7–9] and x-ray [12] experiments, the (11) peak position now corresponds to a lattice constant $b = 4.26$ Å. The (11) peak is also much narrower than observed for the vapor-deposited monolayer [see Fig. 2(a)], corresponding to a larger coherence length in the \mathbf{b} direction of 120 Å.

Profile analysis of the solution-deposited monolayer diffraction pattern shows a better fit [dashed curve in Fig. 2(b)] if the C32 molecules are oriented with the plane of their carbon skeleton *perpendicular* to the surface as illustrated in Fig. 1(c). A parallel orientation of the molecule results in too much intensity for the ($h0$) peaks (solid curve). However, because the ($h0$) peaks are more poorly resolved than for the vapor-deposited monolayer, it is also possible to fit the diffraction pattern of the solution-deposited monolayer with a model in which there are equal numbers of parallel and perpendicular molecules as in Fig. 1(d) [21]. As described below, we are able to test this possibility by comparing the relative intensity of the (11) peaks for the two C32 monolayer phases. Nevertheless, it is already evident that the intermolecular spacing, the molecular orientation, and the monolayer coherence length are strongly affected by the presence of the C7 solvent.

In order to investigate the amount of solvent required to effect the transformation between the two C32 monolayer structures, we performed a series of experiments in which a controlled amount of the C7 solvent was added

or removed from the cell containing the vapor-deposited monolayer. In Fig. 3(a), we have plotted another diffraction pattern of the same vapor-deposited monolayer as in Fig. 2(a). With the addition of only a monolayer equivalent of C7 to the cell, the diffraction pattern [Fig. 3(b)] changed to one similar to that of the solution-deposited C32 monolayer in Fig. 2(b). That is, the d spacing corresponding to the (11) peak is again 4.26 Å, and the peak has narrowed. Upon removal of 0.33 layer of C7 [Fig. 3(c)], the (11) peak broadens and shifts slightly to lower Q . Finally, after heating to 280 °C, virtually all of the C7 was removed and the diffraction pattern [Fig. 3(d)] returned to that of the pure vapor-deposited monolayer, including an enhancement of the ($h0$) peaks at low Q .

Analysis of the diffraction patterns in Fig. 3 allows a further test of the models proposed for the two C32 monolayer phases, since all of the patterns have been obtained with the same substrate and the same amount of C32 in the cell. In Fig. 4, the (11) Bragg peaks of the two different C32 monolayer phases [Figs. 3(a) and 3(b)] have been replotted. The solid curve calculated for the parallel configuration of the molecules in the model of Fig. 1(b) has been scaled to fit the (11) peak of the vapor-deposited monolayer (squares). We have then calculated the profile expected for a (11) peak of the solution-deposited monolayer scaled to the *same* number of C32 molecules. This is done for each of the three models in Figs. 1(b)–1(d). It is apparent that the short-dashed curve corresponding to the model of alternating parallel and perpendicular molecules within a lamella [Fig. 1(d)] gives the best fit to the (11) peak observed from the C32 monolayer in the presence of C7 (circles).

From these results, we conclude that the introduction of less than a monolayer of C7 solvent can result in a

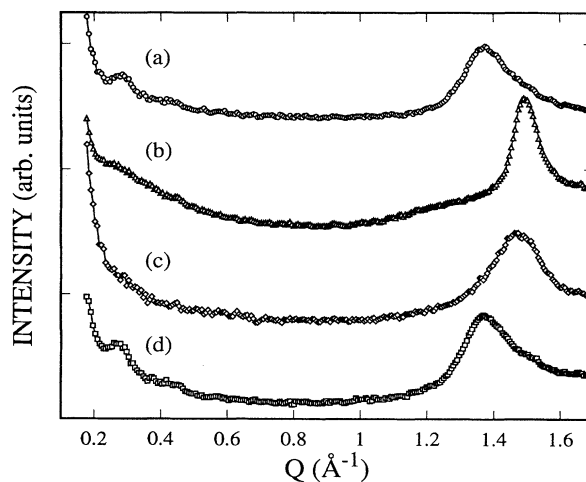


FIG. 3. Dependence of the n -C₃₂D₆₆ monolayer diffraction patterns on the amount of C7 solvent present: (a) the pure vapor-deposited monolayer, (b) after the addition of one monolayer equivalent of solvent, (c) after removal of 0.33 layer of solvent, and (d) after removal of all of the solvent.

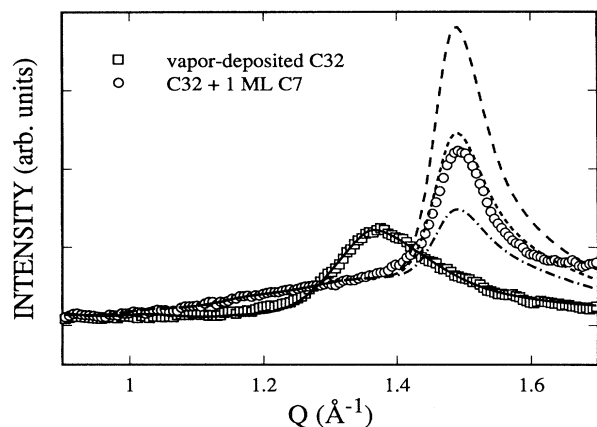


FIG. 4. Plots of the (11) Bragg peaks of the n -C₃₂D₆₆ monolayer as vapor deposited (squares) and in the presence of a monolayer of C7 solvent (circles). Comparison with calculated profiles: parallel model of Fig. 1(b) (solid and dash-dotted curves); perpendicular model of Fig. 1(c) (long dashed); and alternating parallel-perpendicular model of Fig. 1(d) (short dashed). The three calculated curves on the right contain a Gaussian component as in Fig. 2(b).

structural transformation of the C32 monolayer from a rectangular-centered unit cell in which the molecular carbon skeleton is parallel to the graphite surface to one in which there is approximately an equal number of parallel and perpendicular molecules. Neither equilibrium structure completely satisfies the essential feature of molecular registry in Groszek's model. The intermolecular spacing in the vapor-deposited monolayer is too large for long-range commensurability with the graphite surface. In the solution-deposited monolayer, alternate molecules having a *perpendicular* orientation cannot register locally on the graphite basal plane. However, in this case, long-range commensurability with an intermolecular spacing of 4.26 Å is achieved through the closer packing allowed by the alternating molecular orientations. We believe it likely that the *sublattice* of molecules oriented with their carbon skeletal plane *parallel* to the surface does satisfy Groszek's model of local registry. Although our experiments cannot confirm this, such registry minimizes the interaction energy of a single C32 molecule on the graphite basal plane. It is also consistent with the azimuthal orientation of the molecule's long axis observed in STM experiments.

At this point, we can only speculate on the mechanism of the structural transformation induced in the long-alkane monolayer by the short-alkane solvent. Possibly, short-range order within the solvent immediately above the monolayer allows the C7-C32 interaction to compete successfully with both the C32-C32 and C32-graphite interactions to induce the restructuring. Finally, our results suggest the need to assess the structural effects of various solvents used in STM experiments on long-alkane monolayers.

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