A Conformational Phase Transition in a Langmuir Film of an Amphiphilic Azacrown

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Received: May 28, 1998

We have used grazing-incidence X-ray diffraction, X-ray reflectivity, and Brewster-angle microscopy to study an amphiphilic azacrown derivative at the air−water interface. The compound studied has a ring-shaped, flexible core with six alkyl chains attached. As the density is increased, the molecules undergo a phase transition from a face-on structure, with the alkyl tails extending away from the interface, to a thicker edge-on structure, with the tails extending radially away from the core. Concomitant with this rearrangement, the film develops long-range in-plane structural order.

1. Introduction

Amphiphilic rod-shaped molecules at the air−water interface display a variety of structures and phase transitions as a function of temperature and surface density.[1−6] The interfacial behavior of amphiphiles that do not resemble rods has been less-extensively studied. The disc- or bowl-shaped molecules that form columnar liquid crystals[7] comprise a particularly interesting class of compounds. Disc-shaped molecules with a rigid triphenylene core and flexible tails have been observed to form two-dimensional columnar phases with the molecules edge-on to the water surface;[8,9,22,23] the tendency toward an edge-on columnar structure is driven by the strong intermolecular $\pi-\pi$ interaction compared with the weaker attraction between the conjugated core and the water surface. With increasing temperature, the columnar structure has been observed to melt into an isotropic or nematic phase.[9] By contrast, an azacrown derivative with a flexible, polar core self-assembles into a "face-on" structure with the core parallel to the surface and the aliphatic tails extending toward the air.[10] Studies of a similarly flexible compound[11,12] have provided evidence for a lying-down to standing-up transition, in which the vector normal to the core reorients to become parallel to the water interface. We now present measurements of an azacrown derivative (**1**, Figure 1) at the air-water interface in which an edge-on to face-on confor-
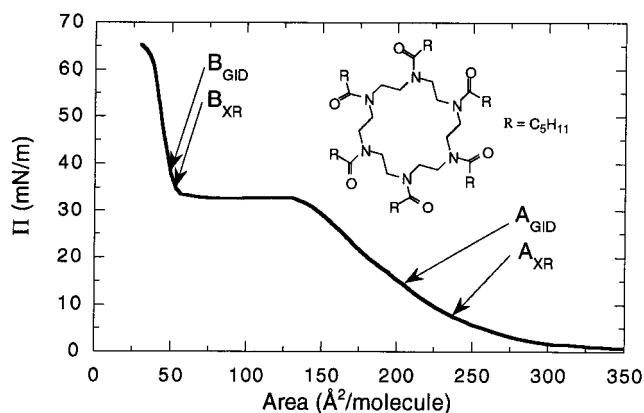

Figure 1. Surface pressure (Π) versus molecular area (A) isotherm of **1** on pure water. A_{XR}, B_{XR} and A_{GID}, B_{GID} are the pressures where the XR and GID measurements were performed. Molecular structure is shown in the inset.

mational change of the molecule is accompanied by the development of two-dimensional in-plane order. The conformational change as a function of spreading pressure Π was studied using synchrotron grazing-incidence X-ray diffraction (GID), X-ray reflectivity (XR), and Brewster-angle microscopy (BAM).

2. Experimental Details

The compound studied was 1,4,7,10,13,16-hexahexanoyl-1,4,7,10,13,16-hexaazacyclooctadecane (**1**). The synthesis,[13] BAM,[14] and X-ray scattering technique[8,9,15] were as described previously. For all film measurements, monolayers were spread from 10^{-4} M chloroform solutions onto pure water. All BAM

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and X-ray measurements were made at 18 °C. GID and XR measurements were performed at beam line X22B of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, with incident wavelength $\lambda = 1.55$ Å.[8,15] The surface pressure varied by less than 9% during the course of each measurement.

3. Pressure−Area Isotherm and Brewster-Angle Microscopy

The flexible central core of **1** incorporates six polar groups which favor a face-on orientation of the molecules at the air−water interface. This is confirmed by the pressure−area isotherm shown in Figure 1, which, consistent with a previous measurement[16] shows an initial rise on compression starting at $A = 320$ Å^2/molecule and terminating at a plateau for areas less than 140 Å^2/molecule. Although other interpretations are possible, this is consistent with a model in which the azacrown lies flat on the water surface and the aliphatic tails gradually reorient from lying flat to extending vertically away from the water surface as the film is compressed. Indeed, if we assume a conformation in which the azacrown core is collapsed on the water surface and the alkyl tails extend away from the water surface and use the known cross-sectional area per alkyl chain of ~ 18 Å^2, then we obtain a minimum molecular area of 108 Å^2. This suggests that in the compressed state, the alkyl chains are almost but not quite vertical. An extended plateau at 32.5 mN/m with a subsequent sharp rise indicates a pressure-driven phase transition. The high-density state certainly cannot correspond to a face-on monolayer structure, since the molecular areas $A < 50$ Å^2 would require unphysically small alkyl chain cross-sections of ~ 8 Å^2. As previously discussed,[16] on the basis of $\Pi - A$ measurements alone one cannot distinguish between competing suggestions for the high-density state: a stable multilayer as recently observed in a similar azacrown derivative[10] or a conformational change of the molecules.[11,12]

Further information was provided by our BAM measurements. For spreading pressures below that of the plateau, we observed a featureless gray pattern. Thus, the low-density phase could consist of a liquid or solid structure formed by face-on molecules, which would be optically isotropic because the molecules have 6-fold symmetry. (On the basis of this observation alone, a liquid structure composed of edge-on molecules could not be ruled out.) Upon nucleation of the solid phase, small grains of solid phase were observed to aggregate in elongated patches or stripes (Figure 2a). The observation of these patches (even after removal of the analyzing polarizer) indicates regions of greater film thickness or density. As the monolayer was compressed across the plateau region, the patches filled a larger fraction of the surface (Figure 2b). Eventually, the solid phase covered the entire surface; however, the monolayer had a grainy or porous appearance since the individual solid grains did not coalesce (Figure 2c). Thus, the BAM measurements suggest that the phase transition at a surface pressure of 32.5 mN/m corresponds to a conformational change of the molecules which results in a thicker monolayer, although they could also be consistent with multilayer formation. Furthermore, the observation of phase coexistence demonstrates that this is a first-order transition, and the noncoalescence of the patches hints at the formation of grain boundaries due to intrapatch structure.

4. X-ray Diffraction and Reflectivity

The scattered intensity in a GID pattern is given by the Fourier transform of the in-plane electron density at the air−water
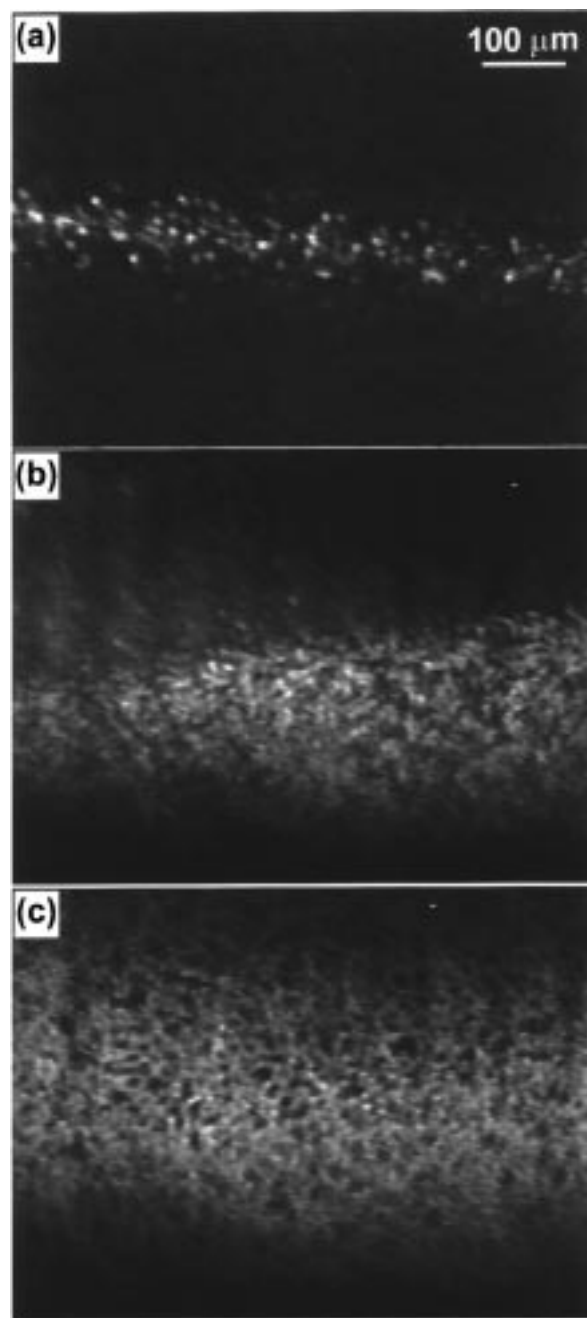

Figure 2. BAM images showing the nucleation and growth of the solid phase as the monolayer is compressed across the plateau region of the isotherm (see Figure 1). The bright areas on the images correspond to regions of greater film thickness or density. (a) At the low density side of the plateau, isolated stripe-shaped aggregates of small solid grains are observed. (b) Toward the middle of the plateau, the stripes increase in size. (c) At the high-density side of the plateau, the surface is covered with the grainy-textured solid phase.

interface.[17] A GID pattern measured at a low pressure of $\Pi = 14$ mN/m (Figure 3b) was featureless, most likely indicating a liquidlike structure of the monolayer. After compression beyond the plateau to 37 mN/m, a broad peak appeared at $q_{xy} = 1.47$ Å^{-1} (Figure 3b), corresponding to a spacing of 4.3 Å. A peak at $q_{xy} = 1.47$ Å^{-1} cannot correspond to a fundamental vector of a hexagonal lattice since the lattice dimensions are far too small. However, the observed spacing of 4.3 Å is close to the core−core spacing in three-dimensional columnar phases of related azacrowns[13,18,19] and indicates that the molecules are most likely "edge-on" to the water surface. This leaves open
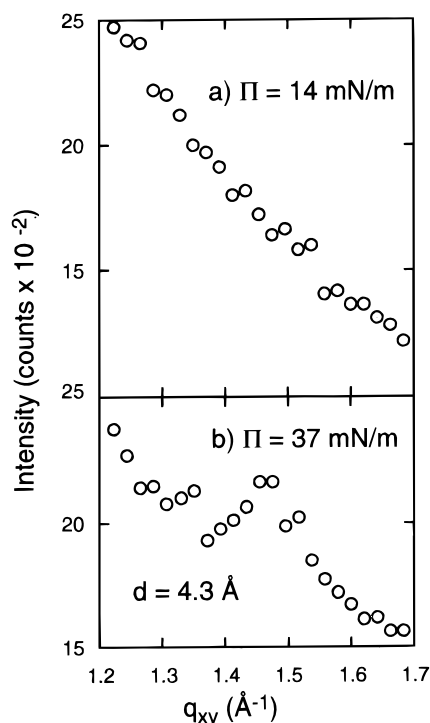
Figure 3. Grazing-incidence X-ray diffraction pattern of **1** measured at (a) 14 mN/m and (b) 37 mN/m. The peak in the bottom panel corresponds to a core−core distance of 4.3 Å.

Figure 4. (a) X-ray reflectivity from **1** at $\Pi = 7$ mN/m. The solid curve shows the best fit to a one-box model ($L = 9.7$ Å, $\rho = 0.30$ e$^-$/Å^3, $\sigma = 3.0$ Å), and the dashed curve shows the best fit to a roughened water interface with no film. (b) X-ray reflectivity from **1** at 35 mN/m. Solid curve shows best fit to a two-box model ($L_1 = 13.9$ Å, $\rho_1 = 0.44$ e$^-$/Å^3, $L_2 = 20$ Å, $\rho_2 = 0.07$ e$^-$/Å^3, $\sigma = 3.1$ Å). In both cases, R/R_F is the measured reflectivity normalized to the Fresnel reflectivity, and insets indicate our proposed molecular conformations.

the question of why we do not observe an additional diffraction peak corresponding to a much larger intercolumnar spacing, as previously observed in 2D columnar phases of triphenylenes.[8] It is possible that our powder averaging was imperfect and that we simply missed the peaks due to the small number of domains. Alternatively, the high-density structure may be a layered edge-on structure without columnar order, similar to that once proposed for the mesophase structure of related azacrowns.[13]

The XR profiles of **1** are determined by the Fourier transform of the gradient of the electron density perpendicular to the water surface;[17] they were analyzed as before[8,20] by modeling the film as a stack of uniform slabs or boxes, each with a different electron density ρ_i and thickness L_i. The solid lines in Figure 4 are the results of least-squares fits to one- and two-box models. Due to the limited compression ratio of the trough used for X-ray measurements, a two-step deposition process was used. Solution was deposited until a pressure of 4m/Nm was achieved. After a short equilibration period, the film was then compressed to a pressure of 8.5 mN/m and the reflectivity was measured. Subsequently, the barrier was retracted, more solution was deposited to a pressure of 26 mN/m, and the barrier was compressed to a pressure of 35 mN/m, at which point a second XR profile was measured. The arrows in Figure 1 were obtained by correlating the pressures determined during the XR and GID experiments with the results of a previously measured isotherm. In a second measurement (data not shown), the pressure after initial deposition was 14 mN/m, and XR measurements were made at 20 and 33 mN/m with no intermediate deposition.

A satisfactory fit to the 8.5 mN/m data was obtained using only one box with a thickness of 9.7 Å and electron density $\rho = 0.30$ e$^-$/Å^3. This density is very close to that of water (0.34 e$^-$/Å^3), but the reflectivity can clearly be distinguished from that expected for a rough water interface (dashed line in Figure 4a). The parameters derived from fits to the reflectivity are somewhat model-dependent, but they are close to those expected from simple physical models of the film. The obtained thickness
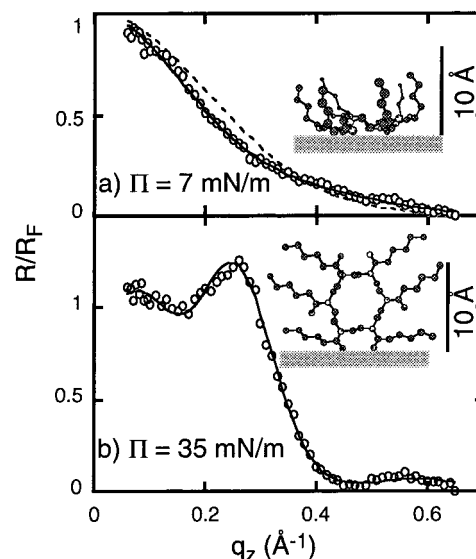
is consistent with the results of simple molecular modeling, which for a face-on structure with the tails directed almost perpendicular to the surface would give a total thickness of 6−8 Å (see inset to Figure 4a). The fitted electron density is actually 30% larger than that calculated from the measured molecular area and may indicate that the monolayer is heavily hydrated in the low-density regime; it is well known[21] that azacrowns similar to **1** are strongly hygroscopic. The data were clearly inconsistent with an edge-on structure, which would require a layer thickness well outside our error bars. The fits to the second data set, measured at 20 mN/m, were qualitatively similar, except that there was evidence of substantial second-layer formation, quite likely induced by the much higher concentration of the initial deposition.

The fitted structure at 35 mN/m is quite different. We could not obtain satisfactory agreement with the data using a one-box model. Using a two-box model, the thickness of the first layer is 13.9 Å and that of the second 20 Å. Molecular modeling of a conformation with the tails fully extended radially from the core would give a disk with thickness 4−5 Å and diameter ∼22 Å, but if we assume instead[8] that the tails closest to the water lie parallel to the interface without projecting into it, exposing the hydrophilic oxygen atoms to the water (inset to Figure 4b), we obtain a layer thickness of 13 Å. Including the results of our GID measurements, therefore, our best model assumes that in the first layer the macrocyclic core is edge-on to the water surface and the tails are all roughly parallel to the water surface. The fitted charge density is within 15% of the calculated value. The second box then corresponds to a partially formed second layer (roughly 22% occupancy) with the chains fully extended in a "sun" configuration. Fits to the second data set, at a point near the left-hand end of the plateau, were quite similar. Given the results from the low-density phase, it seems likely that the second layer observed at high compression was at least, in part, an artifact of the deposition technique, since in both cases the route to the high-pressure phase involved depositing solution at moderately high spreading pressure.

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5. Summary

Isotherm, BAM, GID, and XR measurements demonstrated that low-density monolayer films of azacrown **1** at the air–water interface form a disordered structure with the cores parallel to the water surface. The low-density phase is most likely strongly hydrated. The system displays a first-order face-on to edge-on transition at $\Pi \approx 35$ mN/m with a concomitant development of short-range in-plane structure order.

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