

Multilayer formation in an azacrown [18]N₆ Langmuir film

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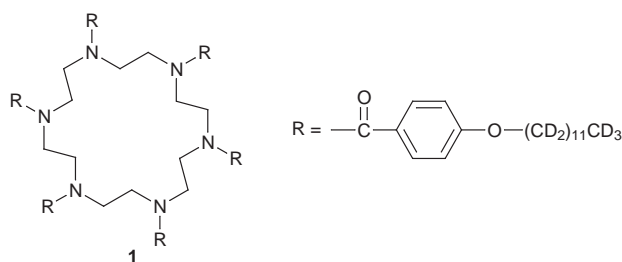
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A neutron reflectivity study of a deuterated azacrown [18]N₆ at the air–water interface shows that it forms multilayers upon compression, with monolayers and trilayers being more stable than bilayers.

Typical Langmuir films are composed of a monolayer of amphiphilic molecules at the air–water interface. Upon compression, they are stable up to an irreversible ‘collapse point’, beyond which three-dimensional droplets are formed and/or the molecules dissolve in the water subphase. Recently, a number of compounds have been shown to form equilibrium multilayers, and in some cases trilayers are more stable than bilayers.^{1,2} In other cases,³ anomalous features in pressure–area isotherms have been associated with structural rearrangements of the molecules themselves.

We have now used neutron reflectivity to study deuterated Langmuir films of 1,4,7,10,13,16-hexakis(4-dodecyloxybenzoyl)-1,4,7,10,13,16-hexazacyclooctadecane **1**.



The bulk liquid crystal properties of **1** have excited considerable interest,^{4–7} due in part to the potential existence of a hollow channel structure and also to the difficulty in distinguishing between columnar and smectic structures. Langmuir films of **1** are also unusual. Published pressure–area isotherms^{5,6,8} measured on compression all show a rise beginning around 200 Å² molecule^{−1}, with an inflection point near 160 Å² molecule^{−1}, followed by a nonequilibrium ‘bump’ at slightly higher concentrations. This feature was variously ascribed to intramolecular reorientations, two-dimensional rearrangement of the film or multilayer formation.

To enhance neutron contrast, the alkyl chains were deuterated. Monolayers were spread at 20 °C from 10^{−3} to 10^{−4} M solutions on Millipore purified H₂O (resistivity 18.2 MΩ cm^{−1}). Neutron reflectivity measurements were made on beamline NG-7 of the Center for Neutron Research at the National Institute of Standards and Technology. After each compression, the film was allowed to equilibrate for 30 min before a measurement was made; each measurement took *ca.* 90 min to perform. Typical reflectivity profiles are shown in Fig. 1. The most dramatic feature is the evolution of a minimum at $Q = 0.11 \text{ \AA}^{-1}$, corresponding to a 60 Å film. This is approximately the thickness expected for a trilayer film. No minimum was ever observed in the vicinity of 0.16 Å^{−1}, as would be expected for a bilayer film.

The reflectivity data were analyzed⁹ by modeling the film as a stack of uniform slabs, or boxes, each with a different scattering length density ρ , thickness L and roughness σ . We used in each case the minimum number of adjustable parameters required to obtain an acceptable fit to the data, with at most two slabs being employed. The profiles resulting from these fits are shown in Fig. 2. The general trends are as follows: at low concentrations, the reflectivity profiles are well described by a single flat slab of thickness 21.4 Å and roughness 3 Å. The thickness and scattering length density are close to those expected for a monolayer film with the central cores in contact with the subphase and the alkyl tails projecting away from the interface. As the concentration is increased beyond 1 molecule per 200 Å², a second well-defined 22 Å layer is formed. However, this layer does not grow to completion. Well before a concentration of 2 molecules per 200 Å² is achieved, the second layer roughens, so that the actual structure consists of a well-defined first layer plus patches of two-layer and three-layer film. At a nominal concentration of 3 molecules per 200 Å², the best fit structure is a rough trilayer film, consisting predominantly of a single sharp monolayer with regions of 1, 2 and 3 layers above that, as shown in Fig. 2.

The ‘slab’ model implicitly assumes that mono- and multilayer regions coexist on short length scales. It is also possible that domains larger than the neutron transverse coherence length are formed, in which case it would be more appropriate to sum reflectivity intensities for the different regions. Our central conclusion, that monolayers and trilayers are more stable than bilayers, still holds in this case, however, since we

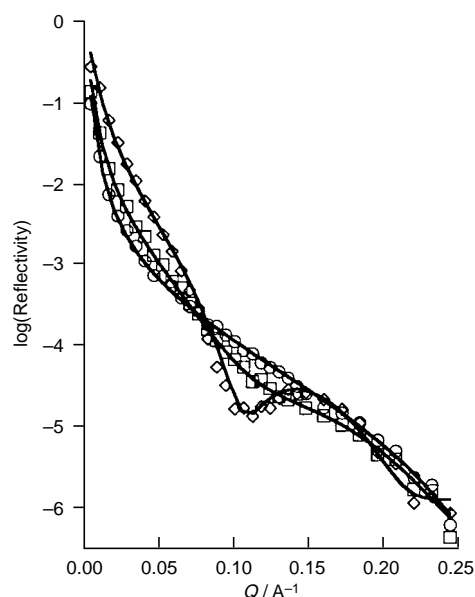


Fig. 1 Log of absolute neutron reflectivity vs. momentum transfer perpendicular to surface for three typical film concentrations of **1**: (○) 1.0, (□) 1.5 and (◇) 3.0 molecules per 200 Å²

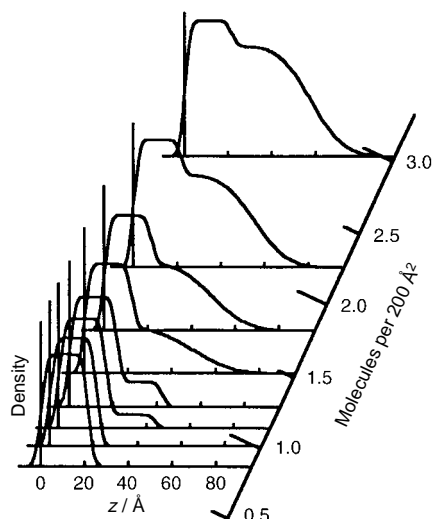


Fig. 2 Density profiles corresponding to 1- and 2-slab fits to the reflectivity data. Scattering length density (arbitrary units) is plotted vs. distance from the air–water interface, at a variety of surface concentrations (scaled to a nominal monolayer coverage of 1 molecule per 200 \AA^2).

never observe the dip at 0.16 \AA^{-1} expected for a bilayer film. We also note that there are systematic uncertainties in the calculated layer thickness, on the order of 15–20%, arising from the assumption of uniform density slabs; models incorporating the possibility of intraslab density variations may yield somewhat different thicknesses.

The relative instability of a bilayer film to trilayer formation most likely arises from the differing character of the hydrophilic amide cores and the hydrophobic hydrocarbon tails. We expect that the molecular orientation should alternate from layer to layer, with the hydrocarbon tails in the first and third tails directed away from the water and those in the second layer directed towards the first layer. The lower interfacial tension between hydrocarbon and air than between hydrated amide groups and air, which is known from X-ray photoelectron

spectroscopy of amphiphilic polymers,¹⁰ should then stabilize the third layer relative to the second.

In summary, we have shown that the nonequilibrium maximum observed in pressure–area isotherms of **1** is the result of multilayer formation upon compression. Furthermore, we have found that a bilayer structure is less stable than either a monolayer or a trilayer structure.

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Notes and References

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