# Adsorption at domain edges

SIR — We recently presented high resolution scanning force microscope (SFM) images of a phase-separated, thin-film surface composed of circular hydrocarbon domains surrounded by a fluorocarbon sea[1]. We have now used these well-characterized films as substrates for preferential adsorption of macromolecules. As shown in the figure, the macromolecules (tobacco mosaic virus, TMV, in this example) are dispersed and readily visible against the distinct background of the phase-separated Langmuir–Blodgett (LB) film. Adsorption occurs preferentially on the fluorocarbon plane, at the juncture between hydrocarbon and fluorocarbon domains. This definitive assignment of binding loci is made possible by the highly localized resolution of the imaging instruments. We can determine distribution and orientation of the adsorbate.

Close inspection of the conformation of the macromolecule reveals that (1) it typically nestles against the hydrocarbon domains, adhering to the side of the domain, (the island-like domain protrudes about 1.5 nm above the surrounding fluorocarbon sea in this particular film); and (2) it can bend around these hydrocarbon islands. Because TMV is a rigid, rod-like structure, the distortion indicates that the adsorption force is strong.

Whereas it is curious that these biological macromolecules lie preferentially
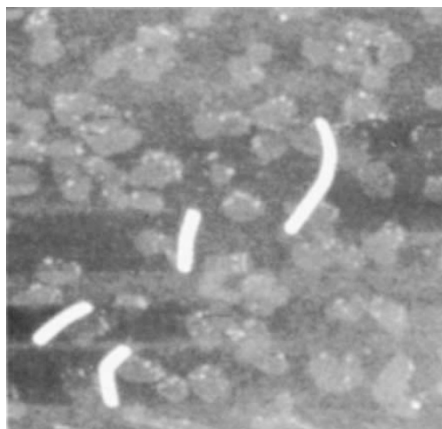


SFM image (1.1 × 1.1 μm²) of TMV adsorbed on to the surface of a mixed hydrocarbon/fluorocarbon LB film. In the background, the lighter, rounded features are the hydrocarbon domains of the phase-separated film; their darker surroundings are fluorocarbon phase[1]. The bright, elongated features are the TMVs; the diameter of their rod-like geometry is about 18 nm (though SFM tip effects widen this dimension somewhat) (D.A., manuscript submitted). Sample prepared by evaporation of a dilute aqueous solution under ambient conditions.

'on' the fluorocarbon surface, their actual location is the juncture between two domains, that is, at a step site. An increase in substrate–adsorbate contact area results from adsorption at a step, a probable contribution to the choice of these sites in the adsorption process.

Another likely source for this selectivity is the ordering of surface energies of the available sites for adsorption. One can regard these phase-separated surfaces as being of three kinds: those terminating in $-CF_3$; $-CH_3$ and $-CH_2-$. Most of the film surface is accounted for by the first two, comprising the terminal methyl groups of the respective carboxylates that comprise the LB film. The third surface is the exposed sides of the hydrocarbon domains, composed of methylene groups. Comparison of the surface energies of the three surfaces indicates that the methylene-terminated surface should present the highest energy surface of the three: the critical surface tensions are 6, 22 and 31 dyn cm$^{-1}$ for $-CF_3$, $-CH_3$, and $-CH_2-$ -terminated surfaces, respectively[2].

The selective adsorption of the macromolecules against the hydrocarbon domains could be explained on the basis of the highest surface energy site available. The selectivity for adsorption at the 'side-walls' has been observed in our laboratory with other adsorbates as well — DNA strands, for example, adsorb in extended conformations. Control experiments of TMV adsorption onto mica, glass, graphite and fully fluorinated surfaces

have produced SFM images dominated by aggregates and rigid-rod conformations.

The image pictured here is obtained in a non-contact imaging mode in which the probe rides about 1–2 nm above the sample surface, avoiding physical contact between probe and sample (ref. 3, and D.A., manuscript submitted). Therefore, the possibility of physical 'placement' of the adsorbate on surface sites by the scanning action of the probe can be eliminated.

This substrate/adsorbate system serves as an example of a crafted surface of heterogeneous yet carefully controlled molecular properties. More generally, the surface could be tailored by the choice of its molecular components to result in well-defined gradients in surface energy, and hence a selective and patterned adsorption.

J. Frommer, R. Lüthi, E. Meyer,
D. Anselmetti, M. Dreier, R. Overney,
H.-J. Güntherodt
*Physics Institute,*
*University of Basel,*
*Klingelbergstr. 82,*
*CH-4056 Basel, Switzerland*
M. Fujihira
*Department of Biomolecular Engineering,*
*Tokyo Institute of Technology,*
*Nagatsuta, Midori-ku,*
*Yokohama 227, Japan*

1. Overney, R. et al. Nature 359, 133–135 (1992).
2. Zisman, W. A. Adhesion and Cohesion (ed. Weiss, P.) 186 (Elsevier, New York, 1962).
3. Martin, Y., Williams, C. C. & Wickramansinghe, H. K. J. appl. Phys. 61, 4723–4729 (1987).

# Errors and ozone measurement

SIR — Mimms[1] recently compared ozone measured using his hand-held TOPS instrument with ozone data from the Total Ozone Mapping Spectrometer (TOMS) on Nimbus 7 and noted possible errors in the TOMS data. The TOMS ozone data used in Mimms's analysis were preliminary and should not have been used for quantitative analysis.

In 1992 the Nimbus 7 orbit had drifted such that we could not measure direct sunlight at the satellite, a measurement needed to maintain the calibration of TOMS to high accuracy. Consequently, between 12 February, when we lost the Sun, and 30 September, when we reacquired it, we were using an extrapolated calibration. These preliminary data are made generally available with a warning that the instrument calibration is not final.

Mimms's analysis in relation to his TOPS measurements showed that TOMS appeared to have as much as +3.7% ozone error. When the final calibration was established for all of 1992 and the final data were processed, we found that the preliminary data had indeed been in error by about +1.7%. The remainder of the

discrepancy appears to have been caused by the effect of Pinatubo aerosols on the TOPS measurement. We recently described the calibration and production of the final TOMS data[2], and confirmed the final calibration of TOMS, through comparison with the world standard Dobson instrument (I83).

Mimms's comparison of his TOPS measurement with TOMS provided a valuable early indication that the extrapolated TOMS calibration was in error. The satellite ozone measurement programme will always need ground measurements to monitor the calibration of the satellite instruments. But we must emphasize that the 'real-time' data we produce and make generally available should be used with caution and that only 'final' data should be used for quantitative ozone analysis.

Richard D. McPeters
James F. Gleason
*NASA/Goddard Space Flight Center,*
*Mail Code 916,*
*Greenbelt, Maryland 20771, USA*

1. Mimms, F. M. Nature 361, 505 (1993).
2. Gleason, J. F. et al. Science 260, 523–526 (1993).