

Report to the beam time SC-4025:

Hierarchical Molecular Self-Assembly of Fluorinated Surfactants at Air-Water and Solid/Air Interfaces

The primary goal of the proposed experiment is to quantitatively investigate how the change in molecular structures determines the structural correlation and mechanics of films incorporating fluorocarbon nanodomains by grazing-incidence small-angle X-ray scattering (GISAXS) at the air-water interface. Systemically, we studied the influence of the fluorocarbon and the hydrocarbon chain lengths ($C_nF_{2n+1}C_mH_{2m+1}$, FnHm) on the domain size and the correlation. Figure 1a shows a typical q -space map of FnHm compounds recorded for F10H18 molecules using 2d detector (Maxipix). The intensity profile along q_y is integrated between the two dotted black lines on the q -space map and represented in black open circles in figure 1b. The experimental intensity profiles were modeled in the framework of the distorted wave born approximation.

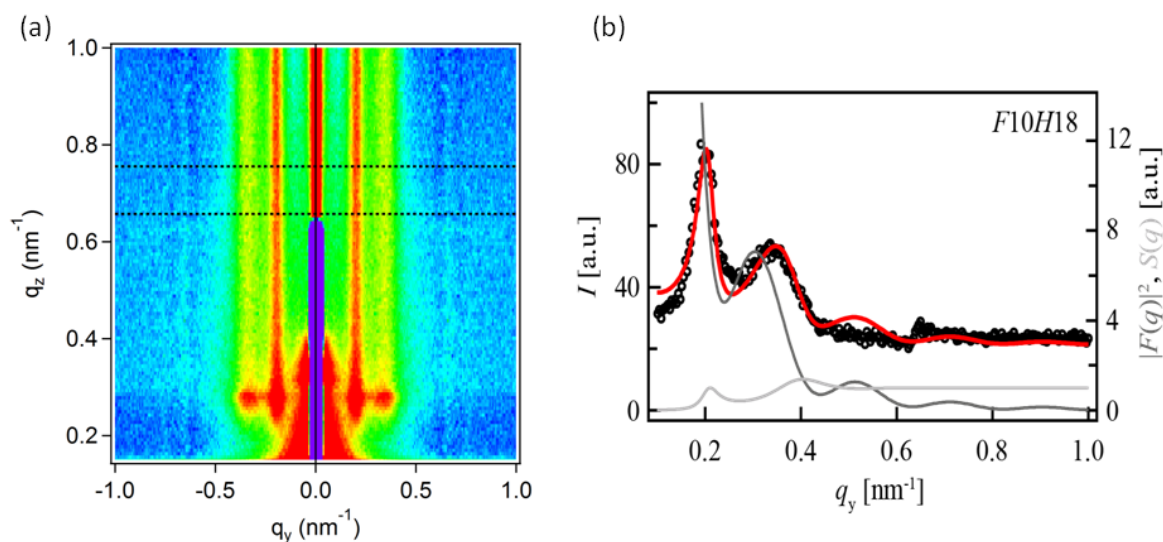


Figure 1. (a) Q -space intensity map of F10H18 measured at surface pressure of 5 mN/m. (b) Intensity profile of F8H18 (black circles). Red thick line represents the fitted intensity, which is composed of the structure factor (dark gray line) and the form factor intensity (light gray line).

However, to extract detailed structural information the form factor of the formed hemimicelles at the air-water interface is modeled using a hemispheroid shape and the structure arrangement of the hemimicelles were modeled using hexagonal configuration within the paracrystal theory. The obtained results are presented in figure 2. The domain size Φ (figure 2a, solid gray circles) of the FnHm hemimicelles increases from ~ 27 to 36 nm with increasing hydrocarbon chain length. Similar tendency was found by increasing the

fluorocarbon chain length, the domain size Φ increases from ~ 29 to 33 nm (figure 2b, solid gray circles).

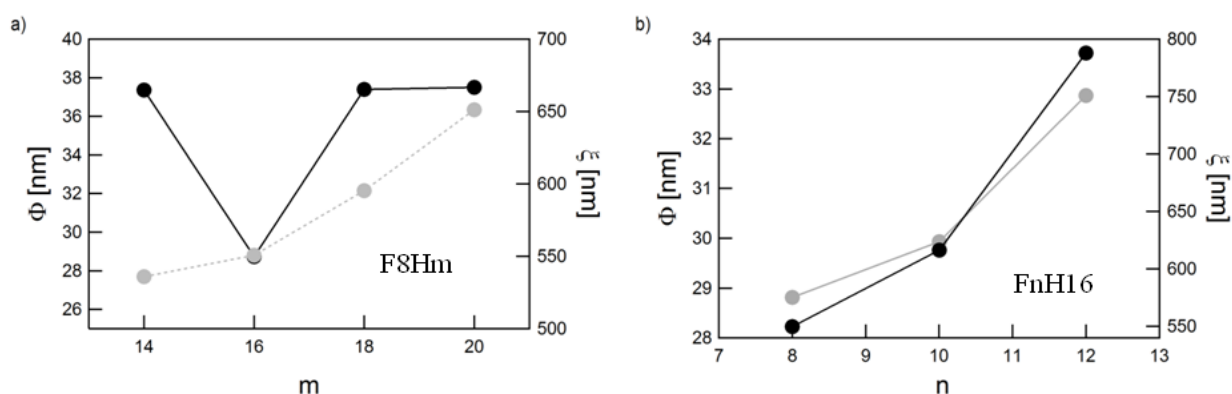


Figure 2. (a) Influence of hydrocarbon chain length on domain diameter Φ (solid gray circles) and on the correlation length (solid black circles). (b) Influence of fluorocarbon chain length on domain diameter Φ (solid gray circles) and on the correlation length (solid black circles).

Moreover, the correlation length between the nanodomain hemimicelles was calculated from the structure factor. The estimated correlation length is found to be ~ 20 times larger than the domain size indicating that the correlation between the hemimicelles can reach up to 20th neighbor. The correlation between the hemimicelles is shown to be more sensitive to the length of fluorocarbon chain length than to the hydrocarbon chain length.

The obtained results clearly demonstrate the influence of chain length on the domain size, correlation of fluorocarbon surfactants. This has high impact on the structure and mechanical properties of the formed nano-sized hemimicelles.