

A VIABLE METHOD OF CHARACTERIZING BROMINE-LABELED LANGMUIR MONOLAYERS

Langmuir monolayers are important interfacial systems for the study of organic, bio-organic, and polymeric amphiphilic macromolecules and their interactions with polar and nonpolar atomic and molecular species. Their numerous biomedical and materials science applications, however, often require localizing the positions of particular molecular, submolecular, or atomic components within the monolayers. Researchers from the University of Pennsylvania and the Brookhaven and Argonne national laboratories, using the CMC-CAT 9-ID beamline at the APS, applied resonance reflectivity to locate resonant bromine atoms that were covalently bound to the hydrocarbon chain of an organic fatty acid in a Langmuir monolayer at an air/water interface.

Although resonance x-ray reflectivity has been used extensively in the structural characterization of inorganic and bio-organic multilayer films, its use with single monolayer films is much more problematic because of the relatively low number of resonant atoms, the small magnitude of the resonant effect, and the lack of periodicity in the samples. Measurements on liquid surfaces are inherently more difficult because interferometric techniques cannot be applied to enhance the diffraction signal from the monolayer. Nevertheless, the development of a resonance x-ray reflectivity technique for the structural characterization of Langmuir monolayers in amphiphilic macromolecules would be of great value because, among other things, it would open the door to localizing resonant-atom-labeled single-amino-acid residues within the scattering length density profiles of monolayers of vectorially oriented proteins.

In the study at CMC-CAT, a monolayer of bromostearic acid was used as a test case to confirm that known resonant atom stoichiometry and location of the monolayer within the chemical structure of the macromolecular species would demonstrate that resonance reflectivity at the air/water interface could specify atomic positions with sub-angstrom precision. Resonance reflectivity requires that the alignment of the liquid surface spectrometer be precisely maintained as the x-ray energy is varied about the resonant atom's absorption edge and that model-independent data analysis techniques be used. Furthermore, accurate measurement of the resonance effect necessitated that x-ray radiation damage of the monolayer film be avoided, even though the small total number of resonant atoms in the monolayer requires long data acquisition times to obtain satisfactory statistics.

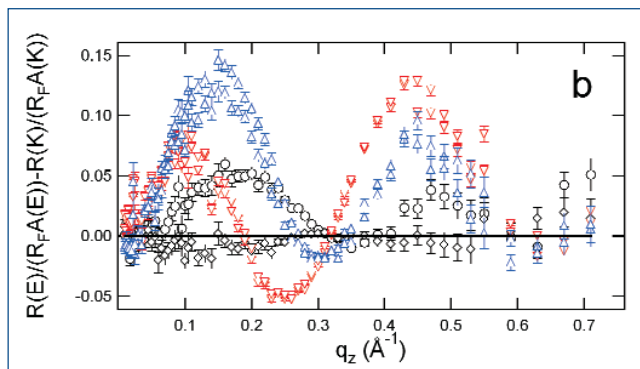
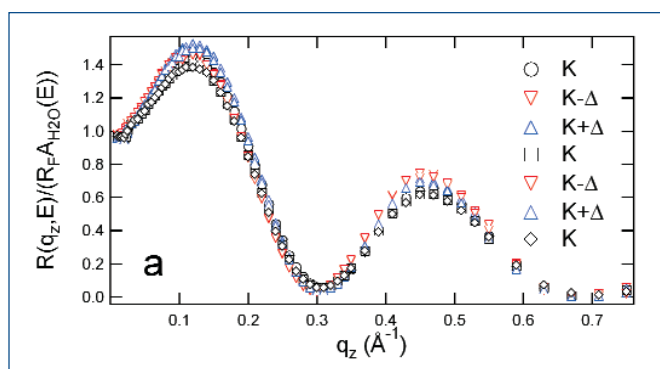
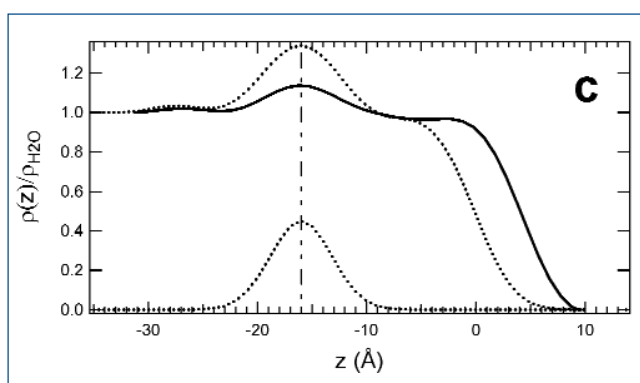


Fig. 1. (a) Fresnel- and energy-normalized reflectivity data collected from a 2-bromostearic acid monolayer at various energies: $K = K_{Br} = 13,474$ eV; $\Delta = 200$ eV. (b) Differences between the second data set at $E = K$ in (a) and the data at $E = K$ reproduce well and indicate that energy-dependent resonant effects exist in the data at $E = K \pm \Delta$. (c) The electron density distributions derived via box refinement for the stearic acid (solid) and 2-bromostearic acid (dotted curve) monolayers. The contribution to the monolayer from Br, as determined from the resonance data, is shown as the lower dotted Gaussian curve, centered at $z = -16.0 \pm 0.2$ Å, with a width of 2.8 ± 0.2 Å. For such small molecules, labeling with Br does not preserve the isomorphism of the monolayer, but for larger molecules such as proteins, substitution of Br for H should not perturb the structure as significantly.



The resonance x-ray reflectivity measurements were performed at CMC-CAT's 9-ID beamline because a constant-exit-height monochromator permits changes in the energy of the beam while keeping downstream optics in alignment. To avoid radiation damage, samples were translated transversely relative to the x-ray beam between data points and between successive scans. The data collection protocol employed cycles through several energies in the vicinity of the Br K absorption edge. The protocol verified that the observed energy dependencies were indeed resonant effects and demonstrated the correct energy dependence of the resonance effect in the brominated sample and the absence of an effect in a control sample without Br. The protocol also confirmed the absence of radiation damage to either sample.

Determination of the Br atom's location within the monolayer profile structure required simultaneous fitting of all available data at different energies. For the analysis to specify the location of the Br atoms with sub-angstrom precision, both the real and the imaginary parts of the changes in the scattering factor, as reported in the literature, needed to be considered.

This study demonstrates the feasibility of combining resonance x-ray reflectivity measurements on Br-labeled Langmuir monolayers with the approaches to data collection and analysis that are required to obtain reliable information on the locations of the resonant species. A best-practice approach would also measure the changes in the real and imaginary parts of the scattering factor directly from the sample, thereby constraining the locations of the resonant atoms even further. — *Vic Comello*

See: J. Strzalka¹, E. DiMasi², I. Kuzmenko³, T. Gog³, and J.K. Blasie¹, "Resonant X-ray Reflectivity from a Bromine-Labeled Fatty Acid Langmuir Monolayer," *Phys. Rev. E* **70**, 051603 (November 2004).

Author Affiliations: ¹University of Pennsylvania, ²Brookhaven National Laboratory, ³Argonne National Laboratory
Correspondence: strzalka@sas.upenn.edu

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THE SURFACE AFFECTS POLYELECTROLYTE-SURFACTANT COMPLEX FORMATION

Understanding the behavior of polymer-surfactant mixtures is important for a host of applications as diverse as detergents, paints, cosmetics, and DNA transfection. Charged flexible or semi-flexible polyelectrolytes (PEs) are a subset of the larger group that contains interesting and useful molecules including DNA and actin. Most studies focused on bulk properties of the mixtures, but researchers at Iowa State University and Hebrew University of Jerusalem took a different approach. Using the MU-CAT 6-ID-B beamline at the APS to perform surface-sensitive x-ray diffraction studies of the gas-liquid interface in PE-surfactant, they discovered that the interface plays an important role in forming these complexes and inducing their aggregation.

The ways in which polymer-surfactant mixtures phase-change, aggregate, and precipitate are not well understood. By measuring surface tension and performing x-ray reflectivity (XR) and grazing incidence x-ray diffraction (GIXD) studies, the researchers examined the role of the surface on the formation of PE-surfactant complexes and investigated how adding salt to the mixture induces crystal formation.

The group experimented using solutions of the PE polydiallyldimethylammonium chloride (PDAC) at 2% by weight in pure water, the surfactant sodium dodecyl sulfate (SDS), and

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Fig. 1. Procedures leading to the crystallization of PE-surfactant complexes. (A) Surface x-ray scattering shows that the polyelectrolyte PDAC (positively charged) at 2% wt. is completely water soluble. (B) Similar studies of SDS (negatively charged) at concentrations smaller than 10^{-4} M show that the surfactant is practically water soluble. (C) By mixing the two solutes, hydrophobic complexes (PE-induced micelles) are formed and detected at the interface. (D) The addition of NaCl to the PE-surfactant mixture solution induces crystallization of cylindrical PE-micelles at the interface.

