

Grazing Incidence XAFS of Lead Adsorbed Underneath Fatty Acid Langmuir Monolayers

Maxim Boyanov,* Alokmay Datta,[†] Tomohiro Shibata,* Jan Kmetko[†], Bruce A. Bunker,* Pulak Dutta[†]

* University of Notre Dame, Notre Dame, IN 46556

[†] Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3112

Introduction

Langmuir monolayers of long-chain fatty acids with divalent metal cations in the aqueous subphase are of long-standing interest, especially as precursors to technologically useful Langmuir-Blodgett films with a considerable degree of structural order [1]. Grazing Incidence Diffraction (GID) of x-rays from synchrotron sources have been used to study the structure of such monolayers. For Cd ions in the subphase GID data from a monolayer at near zero surface pressure show diffraction peaks from an asymmetrically distorted fatty acid monolayer along with weaker peaks from a supercell of the monolayer lattice which have been assigned to a monolayer of Cd ions [2]. However, direct confirmation of the presence of a metal monolayer is lacking, as well as more detailed information about the immediate environment of the metal ions. Preliminary results from grazing incidence XAFS of Zn ions underneath a fatty acid Langmuir monolayer indicate, among other things, a decrease in the Zn coordination number with respect to the bulk value [3] indicating a considerably different microenvironment. GID studies on heneicosanoic acid ($\text{CH}_3(\text{CH}_2)_{19}\text{COOH}$, C21 acid) on a subphase containing Zn ions show peaks only from the fatty acid monolayer [4] whereas some extra peaks similar to those with Cd ions are seen when Pb ions are present in the subphase [5]. In this study, systematic polarization dependent grazing incidence XAFS studies at the L_3 edge of Pb has been carried out on a monolayer of C21 acid with Pb ions in subphase to detect the interfacial adsorption of Pb by the fatty acid monolayer and to selectively probe the in-plane environment of the metal atoms in this thin layer.

Methods and Materials

XAFS studies were carried out at the MRCAT 10-ID beamline at the Advanced Photon Source. The MRCAT beamline is equipped with a cryogenic double-crystal Si (111) monochromator and tunable undulator which allows XAFS measurements over the energy range from 5 keV to over 30 keV. A harmonic rejection mirror was used to eliminate the third and higher x-ray harmonics from the monochromator. The equipment used has been described elsewhere [6]. The x-ray beam at around 13 keV (near the L_3 absorption edge of Pb) was defined to a vertical width of $20\mu\text{m}$ and a horizontal width of 15 mm by slits and was made incident on the monolayer-covered water surface in a Langmuir trough at ~ 0.8 mrad, below the critical angle of water at 13.5 keV to achieve grazing incidence. The trough is an enclosed system with Kapton windows for the incident and scattered x-rays and an inlet and outlet to maintain a slight overpressure of He. This reduces radiation damage of the film. GID data were collected on monolayers as a check on the diffraction pattern and to see the extent of radiation damage suffered by the monolayers. Fluorescence detection mode was used, with 100% Kr in the two detectors which were placed in-plane and vertically above the liquid surface. The two signals are separately collected in slew-scan mode (about 9 min/scan).

About $65\mu\text{L}$ of C21 acid in chloroform (0.9mg/mL) was spread on millipore water (resistivity $18\text{M}\Omega\text{-cm}$) with $\sim 10^{-4}\text{M}$ PbCl_2 dissolved in it. Monolayers were compressed by a constant perimeter barrier to a slight positive surface pressure which was taken to be $\sim 1.0\pm 0.5$ dynes/cm (Balance ST9000, Nima Technology). Temperature was maintained at 9°C by circulating water. The pH of the subphase was either unadjusted (~ 5) or raised to ~ 7 by CsOH. GID checks showed the presence of both C21 acid monolayer peaks and the weak peaks as previously observed [5]. The pattern was found to be stable for about 45 mins under radiation damage. Hence the monolayer was exposed to x-rays for this time during each XAFS scan. Continuous (slew)-scanning mode was used which minimizes the radiation damage to the film. The x-ray penetration depth at the L_3 edge is about 120\AA . Thus the x-rays sampled the monolayer and about 100\AA of the subphase underneath, and there could be some contribution in the XAFS signal from ions in this solution ("bulk" ions).

XAFS data were also collected at grazing incidence for a 10^{-4}M PbCl_2 solution without the C21 acid monolayer, to assess the effect of the fatty acid monolayer on the Pb ions. For calibration standards used in the XAFS analysis, various standard lead compound spectra measured previously at NSLS [7] were used, as well as some taken from the XAFS database [8].

Results and Discussion

In absence of the C21 acid monolayer no fluorescence signal was observed from the PbCl_2 solution. The clear signal obtained from a solution with the same concentration in presence of the fatty acid monolayer is an unequivocal indication that the fatty acid headgroups are causing formation of a dense layer of Pb atoms or ions at the air-water interface. The Fourier transforms (FTRs) of the data are shown in Fig. 1. These correspond to a

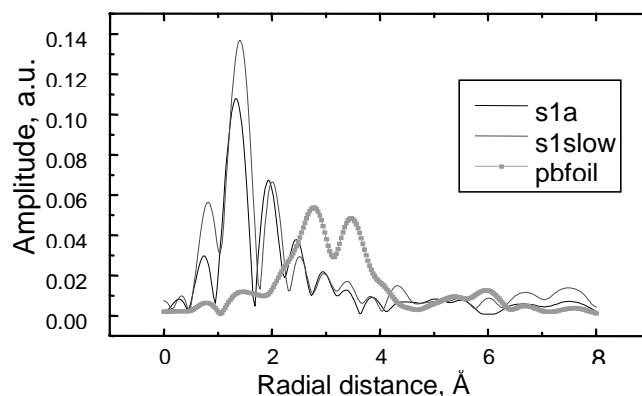


Fig. 1. Fourier transform magnitudes for the PbCl_2 / C21 monolayer sample and for metallic Pb. Data obtained both conventional energy step scans and a continuous slew scan are both shown for the unadjusted pH sample.

C21 monolayer with Pb ions at unadjusted pH, fast (s1a) and slow scans, overlaid with the FTR from a Pb foil standard. The increased amplitude of the first peak of the slow scan is due to remaining background, otherwise the slow and quick spectra are essentially the same. A comparison with the overlaid Pb foil spectra indicates that there is an in-plane Pb-Pb interaction since the polarization of the beam was preferentially sampling the in-plane interactions. However, the signal was also interfering with the fluorescence from the “bulk” ions and the deconvolution of this contribution is underway. As noted above, a comparison of the FTRs of sample and standards is shown in Fig. 1. The only candidates for resemblance of the lower R spectrum are the Pb-acetate and Pb-carbonate. The data were compared with other standards as well (Fig. 2). The bigger amplitude of the first peak is most likely due to the hydration shell signal from the “bulk” ions. The carbonate lacks the peak at 2.5Å present in the data, which confirms that the environment of most of the atoms is carboxylate, as expected. The doublet at 3.0Å and 3.5Å, however, is not present in the Pb-acetate spectrum. Also, its position is close to that of the Pb foil, which strengthens the assignment to the Pb-Pb bond in the monolayer.

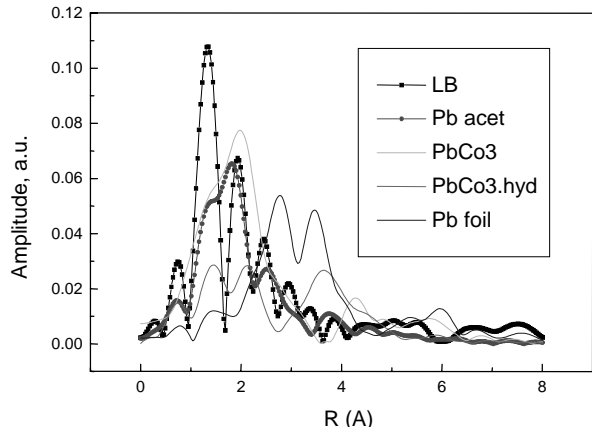


Fig. 2. Comparison of the Fourier transforms of unknown sample and standard compounds: Pb Acetate, PbCO₂, PbCO₂ hydrate, and metallic Pb.

An interesting result is obtained when the pH of the solution is brought to pH=7.0 with CsOH. The spectrum then matches almost exactly that of a PbCO₃-hydroxide (Pb₃(OH)₂(CO₃)₂), – a spectrum obtained from the International XAFS Database. This is shown in Fig. 3. This is probably the result of a chemical reaction at this high pH but the exact interpretation of this spectrum is underway.

Summary and Conclusions

To our knowledge, this is the first systematic grazing incidence XAFS study on divalent metal atoms or ions adsorbed to Langmuir monolayers. Qualitative results have been obtained indicating a Pb-Pb in-plane bond, a carboxyl environment of the majority of the Pb atoms, and a hydration shell signal coming most likely from the “bulk” ions. Quantitative information is being sought by measuring and isolating a signal from Pb-acetate solution and from a pure PbCl₂ solution. It will then be feasible to determine coordination number and distances for the Pb atoms.

Acknowledgments

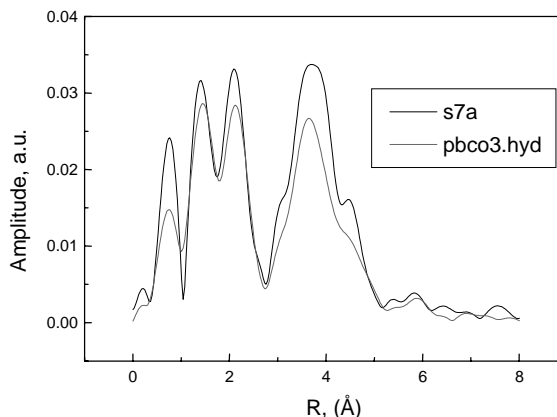


Fig. 3. Comparison of the Fourier transforms of unknown sample and standard compounds: Pb Acetate, PbCO₂, PbCO₂ hydrate, and metallic Pb.

This research was supported in part by the US Department of Energy under grant no.DE-FG02-84ER45125. The work was performed at the Materials Research Collaborative Access Team at the Advanced Photon Source. MRCAT is supported by the U.S. Department of Energy under Contract DE-FG02-94-ER45525 and the member institutions. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, under Contract No. W-31-102-Eng-38.

References

- [1] Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self Assembly*, Academic Press, New York, 1991.
- [2] Böhm, C et al. *Langmuir* **1994**, *10*, 830.
- [3] Watanabe, I. et al. *J. Am. Chem. Soc.* **1997**, *119*, 12018.
- [4] A. Datta et al, unpublished.
- [5] J. Kmetko et al, unpublished.
- [6] Barton, S. W., Thomas, B. N., Rice, S. A., Lin, B., Peng, J. B., Ketterson, J. B., Dutta, P. *J. Chem. Phys.* **1988**, *89*, 2257.
- [7] B. Boyanov, Personal Communication..
- [8] International XAFS Society Database, accessible at <http://ixs.iit.edu/database>.