

## POLARIZATION XAFS STUDY OF IONS AT SOLUTION SURFACE

Soap, when dissolved in water, easily forms bubbles even at millimolar concentrations. Such bubbles surround the included air with a monolayer of soap molecules, as seen for the large fatty acid sodium salt illustrated in Fig. 1. Soap, a typical surfactant, has a strong tendency to come to the surface of an aqueous solution, resulting in a highly concentrated surface density. Surfactant molecules normally possess a long hydrocarbon chain with an ionic head. The hydrophobicity of the long hydrocarbon makes the surfactant insoluble in water, sticking to oily substances instead; the hydrophilicity of the ionic group forces the surfactant molecule adhere tightly to the surface of the aqueous solution.

The molecular packing of the surfactant at the solution surface depends on the identity and concentration of the counter ion; for fatty acid soaps, use of metal ions, such as calcium(II), cadmium(II) or zinc(II), as the counter ion assist in

the formation of a solid monomolecular film (the Langmuir monolayer) at the solution surface. Although the structure varies between the ions, well organized structures including both the fatty acid and the cations must form at the solution surface. As information concerning these surface structures are interesting to colloid and solution chemists in addition to being important in the detergent industry, a large number of thermodynamic and spectroscopic studies have attempted to elucidate this structure. Such studies have utilized laser driven sum-frequency-generation and second-harmonic-generation spectroscopy to address this question, since these techniques are strictly surface sensitive. None of these attempts, however, have yet been able to give the coordination structures of the metal ions at the Langmuir monolayer. Unlike the available methods to study solid surfaces, few techniques exist that are suitable for the study of liquid surfaces.

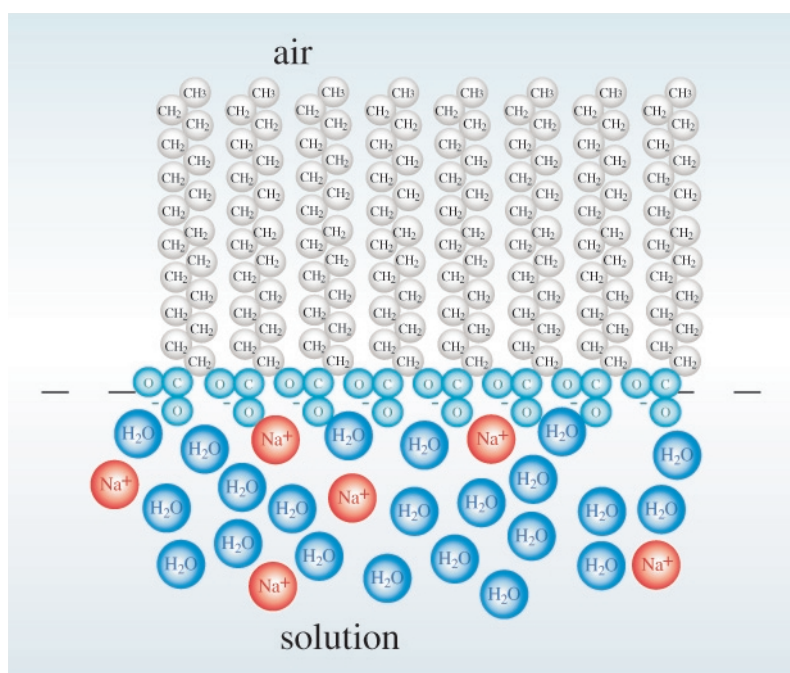


Fig. 1. A schematic model for stearate monolayer structure at the aqueous solution surface.

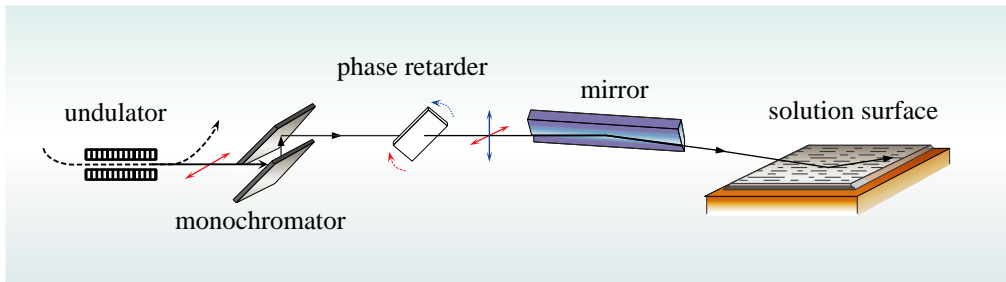


Fig. 2. Total-reflection polarization-XAFS system for the study of solution surfaces at beamline BL39XU.

We are developing a method of X-ray absorption spectroscopy to allow the study of solution surfaces. A monochromatized X-ray beam is introduced onto the solution surface at a small glancing incidence angle to allow the detection of surface elements only, under total-reflection conditions. A high brilliance and small divergence

X-ray beam deriving from the undulator at beamline **BL39XU** is most appropriate for this application.

In addition, the solution surface is a two-dimensional reaction field; the geometry of ions at the surface may preferentially orient with respect to the liquid surface. To describe the coordination structures of ions at the solution surface by the

XAFS method, we require linearly polarized X-rays both parallel and normal to the surface. As the liquid surface cannot be turned upright, a beamline capable of supplying X-rays polarized both horizontally and vertically to the surface is essential for these measurements.

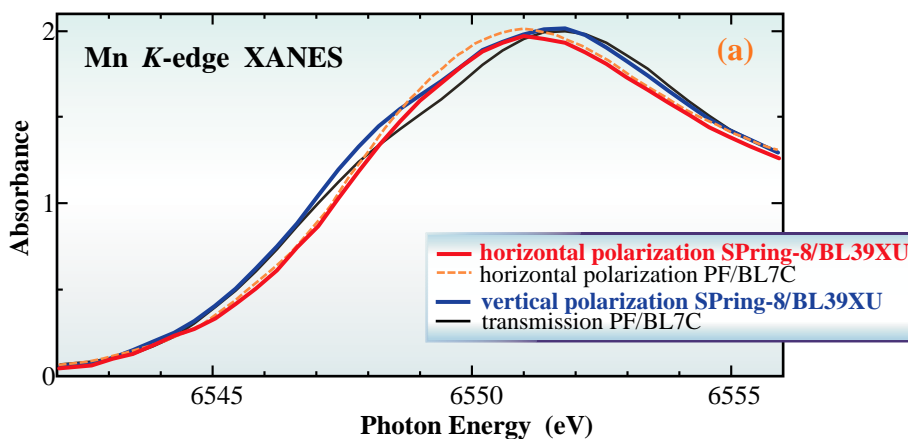
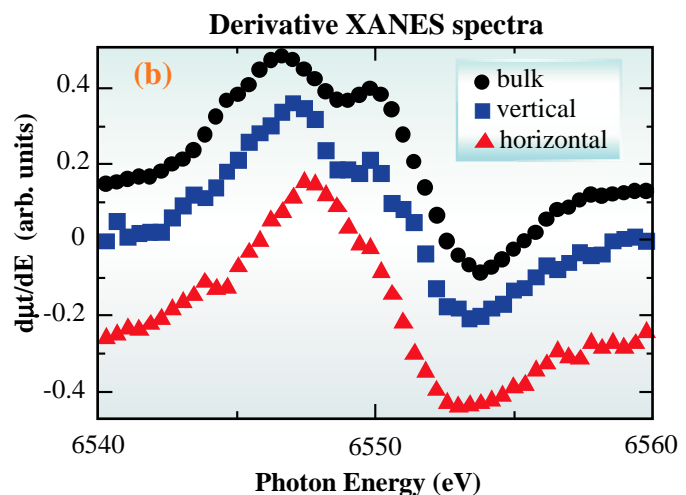


Fig. 3. (a) Mn K-edge XANES spectra for the Mn(II)-stearate monolayer at the aqueous solution surface. (b) The first derivative XANES spectra for Mn K-edge.



The phase retarder at BL39XU, originally installed for X-ray magnetic circular dichroism (XMCD) studies, is also an ideal component for the present study, capable of quickly converting the horizontally polarized X-rays into vertically polarized beams.

The X-rays from the monochromator pass through a diamond crystal phase retarder to be reflected by a silicon mirror (Fig. 2). The mirror is tilted at an angle designed to deflect the beam horizontally at an angle large enough to remove higher harmonics from the double-crystal monochromator; the beam is also deflected vertically at 1 mrad, the total-reflection incidence angle at the solution surface.

The solution cell, described in a previous report [1], contains a sample solution with 1 mmol/dm<sup>3</sup> Mn(II) ion. The solution surface is covered by a monolayer of stearic acid (CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>COOH). We obtained the Mn *K*-edge X-ray absorption spectra using two linearly polarized X-rays (Fig. 3(a)). The vertical polarization spectrum possesses a shoulder at the edge; the horizontal spectrum does not, clearly demonstrated in the first derivative spectra (Fig. 3(b)). In our evaluation of the transmission spectra for bulk Mn(II) solutions, the shoulder

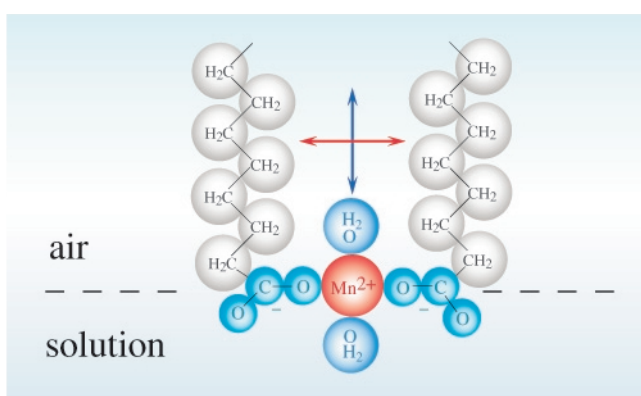


Fig. 4. The proposed coordination structure for the Mn(II)-stearate monolayer at the aqueous solution surface. The polarization directions correspond to the spectra in Fig. 3, respectively.

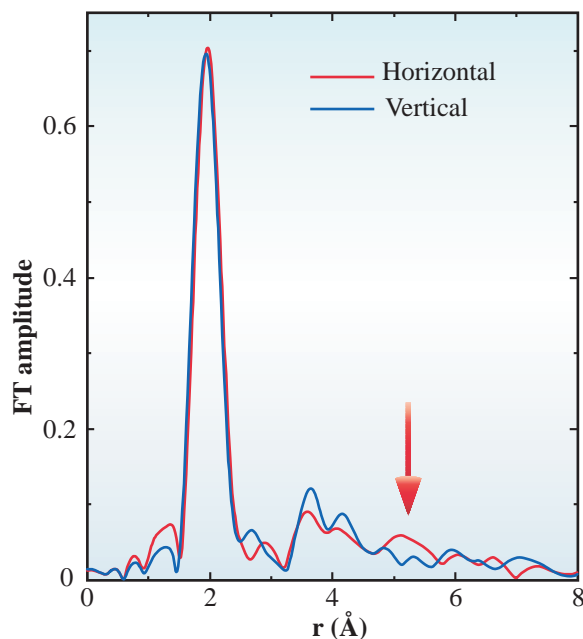


Fig. 5. The Fourier-transformed EXAFS spectra for the Zn(II)-stearate monolayer at the aqueous solution surface.

structure or double peaks in the first derivative are characteristic of such bulk solutions. As the coordination structure of the Mn(II) ion in the bulk solution is octahedral containing six coordinating water molecules, the coordination structure on the vertical axis must be similar to that of bulk one.

Structures in the horizontal plane must differ from the bulk structure. We present a candidate model for such a structure (Fig. 4).

For a Zn(II)-containing solution covered by a monolayer of stearic acid, the two polarization XANES spectra at Zn *K*-edge are similar, yet differ from the bulk one. The spectra clearly indicate that Zn(II) adopts tetrahedral symmetry at the Langmuir monolayer, in contrast to the octahedral structure observed in the bulk [2]. Careful inspection of the EXAFS spectra indicated that a difference between two polarization EXAFS at around 5 Å (Fig. 5); a small peak appears in the horizontal spectrum only. This peak may correspond to the Zn-Zn distance in the

Langmuir monolayer. A distance of approximately 5 Å correlates with that found for zinc acetate in an unhydrated crystal, a structure adopting a layered conformation. Each layer accommodates zinc ions on the same plane, connected by acetate bridges of a 4.8 Å distance. We outline our proposed model for the Zn-stearate Langmuir monolayer in Fig. 6.

This new spectroscopic method is useful for the analysis of liquid surfaces, providing information previously thought to be impossible.

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#### References

- [1] I. Watanabe, H. Tanida, S. Kawauchi, M. Harada and M. Nomura, *Rev. Sci. Instrum.* **68** (1997) 3307.  
 [2] I. Watanabe *et al.*, *J. Am. Chem. Soc.* **119** (1997) 12018.

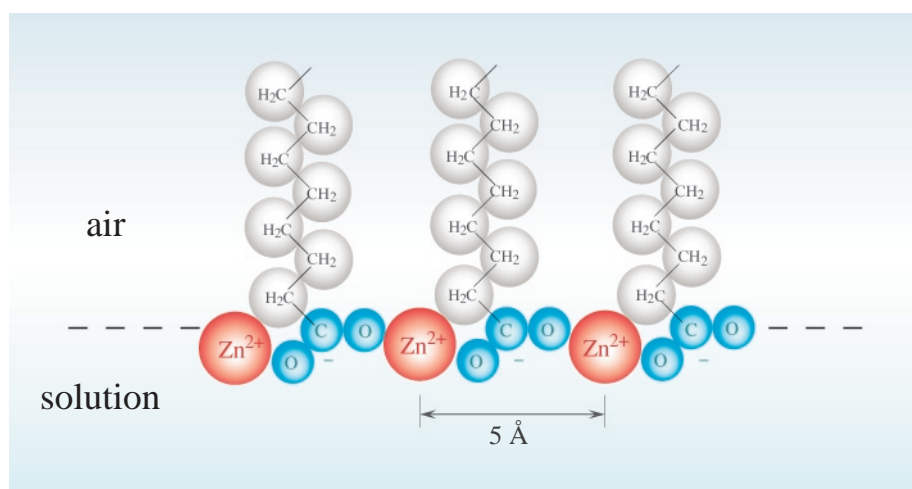


Fig. 6. The proposed coordination structure for the Zn(II)-stearate monolayer at the aqueous solution surface.