

Coordination Structure of Zinc(II) Ions on a Langmuir Monolayer, Observed by Total-Reflection X-ray Absorption Fine Structure

Iwao Watanabe,* Hajime Tanida, and Sigehiro Kawauchi

Department of Chemistry, Graduate School of Science
Osaka University, Toyonaka, Osaka 560, Japan

Received May 6, 1997

It is known that some divalent metal ions, such as Pb(II), Cd(II), and Zn(II), assist condensation of amphiphilic fatty acid at the air/water interface with no surface pressure^{1,2} and that they assist the fatty acid monolayer self-assembly into two-dimensional crystalline structures.³ The condensation effect is not simply due to the electric charge on the ion, because alkaline earth metal ions do not assist in condensation.¹ Self-assembly of the crystalline structure must therefore be driven by the covalent character of the bond connecting the metal ion and carboxylic group.

The crystalline structures have been intensively analyzed by the grazing incidence X-ray diffraction method.^{3–10} It has disclosed very clearly a two-dimensional lattice arrangement in the tail part of the amphiphiles and their tilt angles with respect to the interface. A Langmuir monolayer has also been studied by vibrational spectroscopic methods.^{11–14} However, the role of metal ions in self-assembly and its mechanism are largely unknown. There has been reported an extended X-ray absorption fine structure (EXAFS) experiment of a Langmuir monolayer by Bloch and co-workers, who utilized the fluorescence detection method with total-reflection incidence.^{15,16} They detect a Mn–Mn interaction under the stearate monolayer only when the monolayer is compressed. No other change in the coordination and/or solvation structure of the Mn(II) ion that might be caused by the formation of a Langmuir monolayer could be found.

The present paper reports, for the first time, results from total-reflection XAFS, that the coordination structure of Zn(II) ion beneath the fatty acid monolayer is different from that in the bulk solution.

The technique, total-reflection total-conversion He⁺ ion-yield XAFS (TRTCY-XAFS), has been reported in detail elsewhere.¹⁷

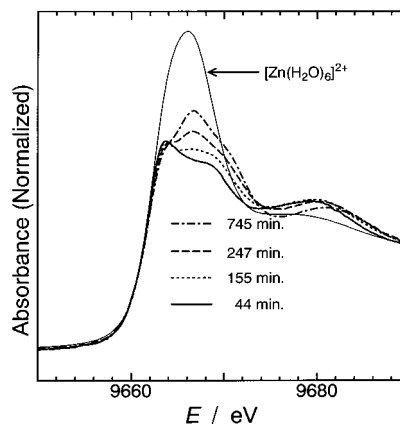


Figure 1. XANES spectra for Zn stearate Langmuir monolayer by TRTCY-XAFS method, at different standing times after the spread of stearic acid on the surface; Zn(II) concentration, 1×10^{-3} mol dm⁻³; solution temperature, ca. 0 °C. The spectrum for Zn(II) hexahydrate by the transmission method is included (thin solid line); concentration, 0.1 mol dm⁻³; solution temperature, ca. 20 °C.

Surface sensitivity was gained by introducing the X-ray beam to the liquid surface at 1 mrad, less than the critical angle for total-reflection. The surface sensitivity was experimentally evaluated to be 8.8 nm,¹⁷ about twice the penetration depth theoretically expected for the evanescent wave.^{3,18} The Langmuir trough was cooled to around 0 °C to reduce the evaporation of water and placed under helium gas. Chloroform was used to spread stearic acid. During the absorption experiments no surface pressure was applied.

The surfaces of ZnCl₂ aqueous solutions with and without anionic surfactants were studied. It was found that 0.1 mol dm⁻³ Zn(II) solution without surfactant gave the same XAFS spectrum as that of Zn²⁺ in the bulk, taken by the transmission method. The same spectrum was also obtained from a dilute Zn(II) solution (5×10^{-3} mol dm⁻³) by segregating the ion at the surface with the aid of 2×10^{-3} mol dm⁻³ sodium dodecylsulfate. This means the coordination structures of Zn(II) at the air/solution interface for both cases are octahedral with six water molecules in the first solvation sphere.^{19,20}

However, when Zn(II) ion is segregated at the surface by stearic acid, its XANES spectrum is quite different. Its white line shown in Figure 1 is smaller in intensity than that of Zn(II) hexahydrate. The hexahydrate displays a strong white line and differs from the complex seen in the Zn stearate monolayer. The white line intensity for Zn(II) is known to be related to its coordination number,²¹ allowing us to estimate the coordination number of Zn(II) at the monolayer to be 4. It was quite a surprise to find a spectral change with elapsed time as indicated in Figure 1. The white line has several components depending on the age of the Langmuir monolayer. After 12 h an equilibrium is reached. The increase in the white line intensity corresponds to an increase in coordination number. EXAFS analysis using our program²² also indicates a variation of coordination structure of the Zn ion with time. The $k^3\chi(k)$ spectra given in Figure 2 demonstrate the structure change after spreading stearic acid onto the solution surface. The $\chi(k)$ data for the monolayer are composed of several components, which differ from that for Zn(II) hexahydrate.¹⁹ Their Fourier-

- (1) Yazdani, M.; Yu, H.; Zografi, G. *Langmuir* **1990**, *6*, 1093.
- (2) Gericke, A.; Hühnerfuss, H. *Thin Solid Films* **1994**, *245*, 74.
- (3) Jacquemain, D.; Wolf, S. G.; Leveiller, F.; Deutsch, M.; Kjaer, K.; Als-Nielsen, J.; Lahav, M.; Leiserowitz, L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 130.
- (4) Leveiller, F.; Böhm, C.; Jacquemain, D.; Möhwald, H.; Leiserowitz, L.; Kjaer, K.; Als-Nielsen, J. *Langmuir* **1994**, *10*, 819.
- (5) Kjaer, K.; Als-Nielsen, J.; Helm, C. A.; Tippman-Krayer, P.; Möhwald, H. *J. Phys. Chem.* **1989**, *93*, 3200.
- (6) Leveiller, F.; Jacquemain, D.; Lahav, M.; Leiserowitz, L.; Deutsch, M.; Kjaer, K.; Als-Nielsen, J. *Science* **1991**, *252*, 1532.
- (7) Gidalevitz, D.; Weissbuch, I.; Kjaer, K.; Als-Nielsen, J.; Leiserowitz, L. *J. Am. Chem. Soc.* **1994**, *116*, 3271.
- (8) Shih, M. C.; Bohanon, T. M.; Mikrut, J. M.; Zschack, P.; Dutta, P. *J. Chem. Phys.* **1992**, *96*, 1556.
- (9) Lin, B.; Bohanon, T. M.; Shih, M. C.; Dutta, P. *Langmuir* **1990**, *6*, 1665.
- (10) Dutta, P.; Peng, J. B.; Lin, B.; Ketterson, J. B.; Prakash, M.; Georgopoulos, P.; Ehrlich, S. *Phys. Rev. Lett.* **1987**, *58*, 2228.
- (11) Simon-Kutscher, J.; Gericke, A.; Hühnerfuss, H. *Langmuir* **1996**, *12*, 1027.
- (12) Kawai, T.; Umemura, J.; Takenaka, T. *Chem. Phys. Lett.* **1989**, *162*, 243.
- (13) Blaudez, D.; Turlet, J.-M.; Dufourcq, J.; Bard, D.; Buffeteau, T.; Desbat, B. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 525.
- (14) Duffy, D. C.; Ward, R. N.; Davies, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 1125.
- (15) Bloch, J. M.; Yun, W. B.; Yang, X.; Ramanathan, M.; Montano, P. A.; Capasso, C. *Phys. Rev. Lett.* **1988**, *61*, 2941.
- (16) Bloch, J. M.; Eisenberger, P. *Nucl. Instr. Methods* **1988**, *B31*, 468.
- (17) Watanabe, I.; Tanida, H.; Kawauchi, S.; Harada, M.; Nomura, M. *Rev. Sci. Instr.* **1997**, *68*, 3307.

(18) Daillant, J.; Bosio, L.; Benattar, J. J.; Blot, C. *Langmuir* **1991**, *7*, 611.

(19) Muñoz-Páez, A.; Pappalardo, R. R.; Sánchez Marcos, E. *J. Am. Chem. Soc.* **1995**, *117*, 11710.

(20) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.

(21) Pan, H. K.; Knapp, G. S.; Cooper, S. L. *Colloid Polym. Sci.* **1984**, *262*, 734.

(22) Sakane, H.; Miyayama, T.; Watanabe, I.; Matsubayashi, N.; Ikeda, S.; Yokoyama, Y. *Jpn. J. Appl. Phys.* **1993**, *32*, 4641.

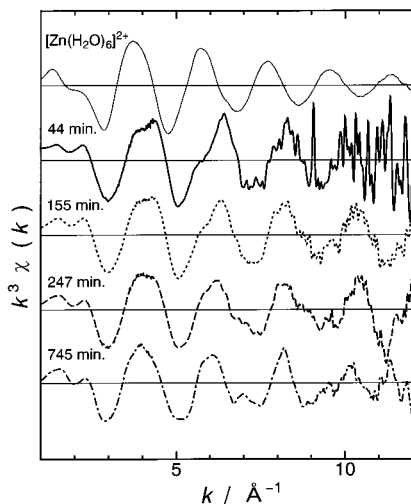


Figure 2. The $k^3\chi(k)$ spectra for Zn hexahydrate and Zn stearate Langmuir monolayer. The conditions are the same as in Figure 1.

transformed spectra are given in Figure 3. The FT spectra have a peak at around 2 Å, which is attributed to a Zn–O bond. Curve fitting analysis on this peak for the 44 min old layer resulted in a distance of 1.96 Å, which is shorter than for the hexahydrate of 2.08 Å. The analyses on older layers indicate a gradual increase in the Zn–O distance corresponding, in agreement with the change in white line intensity, to a change in coordination number from 4 to 5, since the bond length is known to increase with the coordination number.²¹ Although the curve fitting analysis is a less reliable way to determine the coordination number, the analysis again predicts the increase in coordination number with time. The XAFS spectra obtained by spreading stearic acid at 75 or 50% of a monolayer demonstrate similar features as those for the complete monolayer surface.

There are other components in the FT spectra between 3.2 and 4.2 Å, which are not discernible in the spectra for ZnCl₂ aqueous solution, crystalline Zn acetate dihydrate, or its aqueous solution. The peak at around 3.8 Å for the 44 min old monolayer is too intense to be attributed to a single scattering process. From Zn carboxylate models, it is possible that this peak corresponds to Zn–C (the first carbon in hydrocarbon chain) atomic coupling enhanced by the forward scattering effect

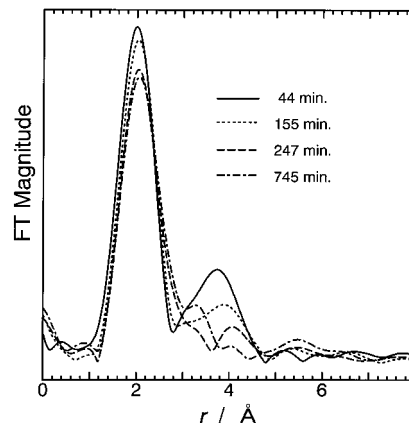


Figure 3. Fourier-transformed spectra for Zn stearate Langmuir monolayer by the TRTCY-XAFS method, at different standing times after the spread of stearic acid on the surface; Zn(II) concentration, 1×10^{-3} mol dm⁻³; solution temperature, ca. 0 °C. The phase shift and back-scattering amplitude values are corrected for oxygen.

of an intervening carbon in the carboxylate. This peak shifted to longer distances and became less intense with time. At last it disappeared and a new component at around 3.2 Å appeared. One of the candidates for this is a Zn–C (the center carbon in carboxylate) distance with an aligned structure of Zn–O–C. (Both O and C are contained in the same carboxylate.)

In conclusion, this study confirms that the Zn(II) ion segregated at a fatty acid Langmuir monolayer takes a tetracoordinate structure at the beginning and later deforms very slowly to a pentacoordinate structure. The process does not need an applied surface pressure. Unless multiscattering calculations for better models are available, it seems difficult to obtain further progress on the structure analysis using the present TRTCY-XAFS data.

Acknowledgment. We thank Dr. Masaharu Nomura of Photon Factory, National Laboratory for High Energy Physics, Tsukuba, for his technical assistance with the incorporation of the TRTCY-XAFS apparatus into BL-7C at Photon Factory. This work has been performed under the approval of the Photon Factory Advisory Committee (Proposal Nos. 94G220 and 96G181) and was supported by a Grant-in-Aid for Scientific Research (no. 05453057).

JA971458C