THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

pubs.acs.org/JPCB

Molecular Rearrangement in a Zinc Stearate Langmuir Film Dependent on a Film Preparation Method Studied Using Polarization-Modulation Infrared Reflection Absorption Spectroscopy and X-ray Absorption Fine Structure

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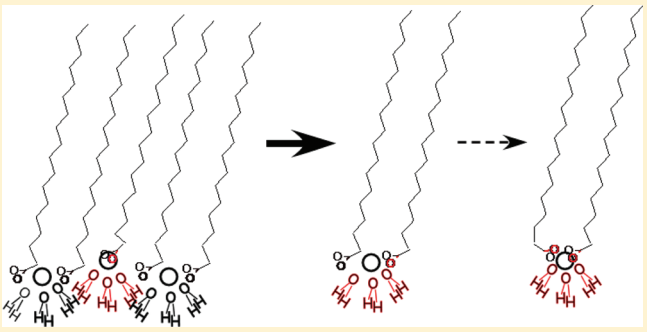
ABSTRACT: Molecular dynamic rearrangement in a Langmuir (L) film of zinc stearate in a cross section image has been analyzed by employing polarization modulation infrared reflection spectrometry (PM-IRRAS) and X-ray absorption fine structure (XAFS). The number of coordination on a zinc cation is evaluated by XAFS, and the coordination structure of the carboxylic group is revealed by the IR analysis. An L film prepared at a fixed area without using film-compression bar exhibits time-dependent change of the coordination structure about a zinc cation, and it attains a highly ordered coordination structure in the carboxylic group region. However, an L film prepared by the Langmuir technique using a compression bar exhibited ignorable spectral changes in both IR and X-ray analyses. The hydrocarbon chains in the compressed L film are better uniformed than the uncompressed film, but the uniformed molecular arrangement of the carboxylic group is restricted to be rearranged, and it does not attain a stable structure in terms of coordination on the zinc cation.



■ INTRODUCTION

The full cross-section image of a Langmuir (L) film (spread monolayer on water) across the air/water interface is difficult to illustrate based on experimental data. The molecular arrangement and orientation in the L film are determined by a balance of at least following factors: crystallization of the hydrophobic part, hydration about the hydrophilic part, and ionic interaction between the film compound and the ion involved in the subphase aqueous solution. The monolayer structure, however, cannot be determined by only the chemical constituents but by physical parameters such as temperature and the surface pressure of the film. Another influential parameter that should be emphasized in this paper is the preparation technique of the L film. After the pioneering works by Pockels and Rayleigh,[1,2] L films are usually prepared by using a compression bar (moving barrier) placed on the brim of the trough across the surface of the subphase solution, and the compressing (shrinking) the surface area of the film controls the molecular density and the surface pressure. During this compression process, molecules adsorbed at the water surface are rapidly arranged to be of 2D crystallites keeping the monolayer thickness.

L film should, however, be intrinsically defined as an aggregate of amphiphilic molecules after the Langmuir adsorption at the water surface, which requires no film compression. When the film molecules are interacted with metal cations in the subphase to form a salt, in particular, the molecular aggregation becomes stronger. For example, cadmium stearate is known to aggregate strongly with no aid of a compression bar to form stiff molecular domains immediately after spreading a stearic acid solution on an aqueous solution involving cadmium ion.[3]

The molecular rearrangement after the Langmuir adsorption has, thus far, never been spectroscopically discussed in a cross-section picture. No significant difference is empirically expected between the compressed and uncompressed L films. If a very long period of time would be spent, the two films would attain a common thermodynamically stable structure. To investigate the role of the coordination and hydration structures about a cation cooperated with the hydrocarbon chain interaction; however, a total analysis across the cross section of the L film is necessary.

Representative techniques for analyzing the molecular structure in an L film in situ are the X-ray diffraction (XRD) technique,[3] infrared external-reflection spectrometry,[4−7] and Raman spectrometry using the attenuated total-reflection (ATR) geometry.[8] XRD is useful when the molecular packing is ordered, and it provides both in-plane and out-of-plane intermolecular distances with a

Received: December 13, 2011
Revised: January 18, 2012
Published: February 16, 2012

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high accuracy, which depict an apparent molecular arrangement in the L film. The IR and Raman techniques provide rich information on molecular conformation and orientation in the film regardless of the degree of the crystallinity. Although these spectroscopic techniques are quite useful, they reveal the structural information only of the film molecules, and no information is given for the ions interacted with the film molecules.

For the purpose of analyzing chemical atmosphere about an ion, X-ray absorption fine structure (XAFS) plays an important role.[9−12] XAFS spectra are conveniently discussed by separating into two regions called X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions. The XANES region that appears near the absorption edge measures an X-ray absorption due to transitions from an electronic core level to unoccupied levels, which reveals the local electronic structure about the ion. The prominent absorption band at the edge is called the white line and it accompanies some informative peaks about the coordination structure. However, the EXAFS region in a higher energy range than XANES measures energy-dependent variation of the excitation probability (absorptivity) due to the interference between the electromagnetic wave going out from the atom generated by the core−electron excitation and the scattered electrons by surrounding atoms. In the case of Zn^{2+} analysis, the white line of XANES is known to respond to the coordination number about the ion,[13−15] which is a fortunate condition for highly sensitive measurements. In the present study, therefore, XANES spectra measured at the air/water interface have been analyzed to reveal the structure on a cation coordinated with water and stearic acid molecules.

In a previous study,[16] Watanabe et al. were interested in the molecular aggregation (surface condensation) effect induced by zinc cation on an L film of stearic acid. Because alkali metal ions are known to exhibit no assist for the molecular aggregation, the aggregation caused by zinc cation suggests that it is not driven only by electric charge. They focused on the coordination structure about zinc cation at the interface of the L film and water. Through the analysis of the XANES spectra, they found that the white line developed with time, which suggested that the coordination number increased. In the discussion of the study, the time-dependent variation was attributed to metal complex formation as a bottleneck. The discussion is, however, based on the chemical information about the zinc cation only, and the correlation with the structure of the fatty acid is still unclear.

In the present study, the IR and X-ray techniques were cooperatively employed to understand the correlation between stearic acid and zinc cation. Both spectra exhibited time-dependent variations, through which the molecular dynamic rearrangement after the film preparation has first been revealed as a function of the preparation technique.

■ EXPERIMENTAL SECTION

Chemicals. Octadecanoic acid (stearic acid) with a purity higher than 99% was purchased from Sigma-Aldrich (St. Louis, MO), and it was used as received without further purification. For preparation of Langmuir (L) films, a chloroform solution of stearic acid at a concentration of ca. 1.0 mg mL^{-1} was used. The solvent, chloroform, was a spectra grade reagent purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan).

L films for the PM-IRRAS measurements were prepared on a USI (Fukuoka, Japan) Langmuir−Blodgett film trough with a size of 97 × 300 × 5 mm^3 by spreading the chloroform solution on a zinc bromide aqueous solution at a concentration of 1.0×10^{-3} mol L^{-1} at pH of ca. 6, which was a good condition to make all of the stearic acid molecules reacted with zinc cations to form zinc stearate as shown later. The trough was placed in an external-reflection optics designated for the FTIR spectrometer equipped with a PM-IRRAS accessory. The subphase water was obtained by a Millipore (Molsheim, France) Elix UV-3 pure-water generator and a Yamato (Tokyo, Japan) Autopure WT100U water purifier, which is a compatible model with Milli-Q. The water exhibited a high electric resistivity higher than 18.2 MΩ cm and the surface tension was 72.8 mN m^{-1} at the temperature, which guaranteed that the water was organic contaminants free.

Two Types of a Langmuir Film Used for the Present Study. Two types of an L film were used for the present study: uncompressed and compressed L films. The uncompressed L film was prepared by spreading the stearic acid solution on a fixed surface area of the zinc bromide aqueous solution using no compression bar. The volume of the spread solution was designed, so that the average molecular cross-section area of the L film would be 0.2 nm^2 that corresponds to the full molecular packing with a perpendicular molecular stance to the water surface.[17] The surface pressure of the uncompressed L film 10 minutes after the preparation was less than 15 mN m^{-1}. Unfortunately, however, the precise monitoring of the surface pressure for a long time period during the IR measurements is difficult because the water-level change due to the evaporation makes the monitoring disturbed. Therefore, it should be noted that the molecular density is kept unchanged through the experiments.

However, the compressed L film was prepared in a usual manner of the Langmuir technique using a compression bar. After the L film was once compressed to attain 15 mN m^{-1}, the surface area was fixed.

PM-IRRAS Measurements. The IR spectra of the L films were measured by using polarization-modulation infrared reflection absorption spectrometry (PM-IRRAS), which is powerful to effectively reduce the absorption bands due to ambient water vapor. The main bench of the PM-IRRAS measurements was a Thermo Fischer Scientific (Madison, WI) Nicolet 6700 FT-IR spectrometer. The FT-modulated IR ray was led out of the spectrometer, and it was passed though the photoelastic modulator (PEM) with an intrinsic resonance frequency of 50 kHz generating alternately s- and p-polarization rays operated by a HINDS Instruments (Hillsboro, OR) PEM-90 PEM controller. The double-modulated (interferometer and PEM) IR ray was directly introduced onto the L film, and the reflected ray was led to an MCT detector liquid-nitrogen cooled through an IR transparent KBr lens. No mirror was used in the optics to prevent disturbance of polarizations. The angle of incidence was 76° in accordance with the optimal conditions analyzed in former studies.[18,19] The half-wave-retardation frequencies were 2900 and 1404 cm^{-1} for the measurements of the C−H and fingerprint regions, respectively.[19−21] The modulation frequency of the interferometer was 20 kHz, and the band resolution was 8 cm^{-1}. The accumulation number of the interferogram collection was 3000 to improve signal-to-noise (SN) ratio,[22] which took about 2000 s.

Bandpass filters were used to remove an excess IR energy that can make the L film move around on water.[20,21] The filters were Spectrogon (Täby, Sweden) BBP-2800−3800 nm and LP-5100 nm IR filters, and they were set on the automatic filter exchanger equipped in the spectrometer.

The ordinate scale of PM-IRRAS spectra does not have a unit of absorbance, but it is given by the ratio of $\Delta S/S(0)$. For the details of the notations, reader may refer to earlier references.[18,22,23] The ratio provides the surface selection rule of PM-IRRAS on water. In the present case, the surface selection rule as a function of the orientation angle can roughly be summarized as follows: the positive band develops when the transition moment is getting close to parallel to the surface.[19,20]

Polarized Total-Reflection Fluorescence XAFS Measurements. For the measurements of XANES spectra of the zinc cation in the vicinity of the monolayer surface, the polarized total reflection fluorescence XAFS technique[11] was employed. Zn K-edge absorption measurements require X-ray of about 9.6 keV, which is far from the resonance position of water. When the energy of electromagnetic wave is much higher than the resonance position, the complex refractive index, $\tilde{n} = n + ik$, is redefined in the X-ray absorption spectroscopy manner as:[24]

$$\tilde{n} = (1 - \delta) - i\beta \quad (1)$$

Here, δ of water is a positive but a very minute value as much as 2.4×10^{-6} at 9.6 keV. The real part of the complex refractive index is therefore very slightly less than unity. In other words, the refractive index of the air phase ($n = 1.0$) is slightly larger than that of water, which enables us to employ the total-reflection configuration at the air/water interface to generate evanescent electric field in the water surface. For the total reflection, the critical angle of water measured from the water surface is calculated to be 2.2 mrad. In the present study, the angle of incidence was set to 1.2 mrad for allowing an extra angle. Zinc cations near the water surface are excited by the evanescent field, and fluorescence X-ray is emitted from the ions. The emitted X-ray was detected by an ORTEC (Oak Ridge, TN) 19-element Ge solid-state detector placed beside the Langmuir trough.

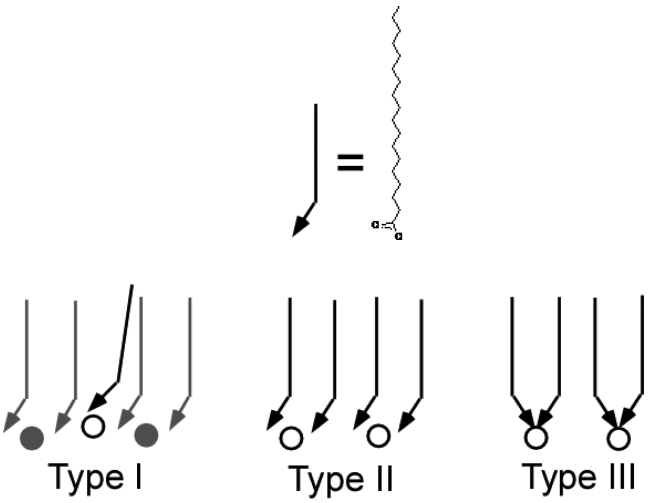
The temperature of the XAFS measurements was fixed at 16 °C. The Langmuir trough with a size of $220 \times 220 \times 2$ mm^3 was made of PTFE. To make the water surface free from breeze, an acrylic cover was placed over the trough. The cover had two X-ray windows made of polyimide (Kapton) with a thickness of 0.050 mm. The X-ray source was the beamline BL39XU, SPring-8, Hyogo, Japan. A diamond phase retarder was used to switch the polarization of X-ray.

■ RESULTS AND DISCUSSION

Uncompressed L Film. An L film of stearic acid was prepared by spreading the monomer solution on the subphase water containing zinc ion without using a compression bar to keep the surface area fixed. With this uncompression technique, the L film at an early stage is expected to have some portions of less ordered molecular aggregates that are schematically illustrated as Type I in Scheme 1. The less-ordered portions are expected to have an electronically unstable interaction with zinc cations at the film/water interface, but it would be a useful model to discuss IR spectra.

Time-dependent PM-IRRAS spectra of the uncompressed L film are presented in Figure 1. The measurements were performed at 16 °C, which is the same temperature as that for the XAFS measurements. After the repeated measurements, it was confirmed that no band was recognized at ca. 1700 cm^{-1} (not shown), which indicated that the stearic acid molecules were fully reacted with the zinc ions at the monolayer to form a zinc salt. In fact, the antisymmetric and symmetric COO^- stretching vibration ($\nu_a(COO^-)$ and $\nu_s(COO^-)$, respectively) bands turn out in the spectra at 1539 and 1404 cm^{-1}, respectively. The L film has an interesting character that all the spectra accompany the band at 1558 cm^{-1} beside the main band at 1539 cm^{-1}.

Scheme 1. Schematic Arrangement of Ionic Species: A Bar and an Arrow Respectively Denote Hydrocarbon Chain and the Carboxylic Group of Stearic Acid, whereas the Open Circle Indicates the Zinc Cation[a]



[a]The hydration structure is eliminated from this illustration.

To study the $\nu_a(COO^-)$ band, an infrared ATR spectrum of a collapsed L film of zinc stearate was measured as presented in Figure 2. The film for the ATR measurements can be considered as an unoriented bulk sample. Because an ATR correction[25] has already been made on the spectra, the peak positions can directly be compared to those measured by PM-IRRAS. The antisymmetric and symmetric CH_2 stretching vibration ($\nu_a(CH_2)$ and $\nu_s(CH_2)$, respectively) bands appear at 2917 and 2848 cm^{-1} respectively, which indicate that the molecules have highly ordered hydrocarbon chains with the all-trans zigzag conformation.[20] The ordered crystallite is made of divalent zinc cation and monovalent stearate anion with the molar ratio of 1:2, which makes the zinc salt electrically neutralized. The ATR spectra of the crystallite gives the $\nu_a(COO^-)$ vibration band at 1538 cm^{-1} as shown in part b of Figure 2. This band position, which is known to be a good marker of a bidentate coordination of stearic acid on a zinc cation,[26] reproduces the major band at 1539 cm^{-1} in the PM-IRRAS spectra. Because the band position sensitively responds to the electronic state of the carboxyl group,[27] the band at 1539 cm^{-1} in the PM-IRRAS spectra reveals that a major portion of the L film is reacted with zinc cations stoichiometrically as in the solid crystal.

According to Bellamy,[28] the band position is shifted to a higher wavenumber by a decrease of the electronic charge density on the ionized carboxyl group. Therefore, the sideband at 1558 cm^{-1} supports that the interacting molar ratio of the zinc ion to stearate is not 1:2, but 1:1 via the monodentate structure.[26] Although the 1:1 association has a poor electric balance, the association should meta-stably and temporarily be generated when a divalent cation approaches the nonuniformed portion of the monolayer on water (Type I). In this manner, the band at 1558 cm^{-1} is a marker to indicate that the L film has nonuniformed portions.

The L film at 16 °C exhibits another notable character: the band at 1558 cm^{-1} decreases with time, whereas a new band at 1520 cm^{-1} appears. In a crystallite of a fatty acid, the molecules

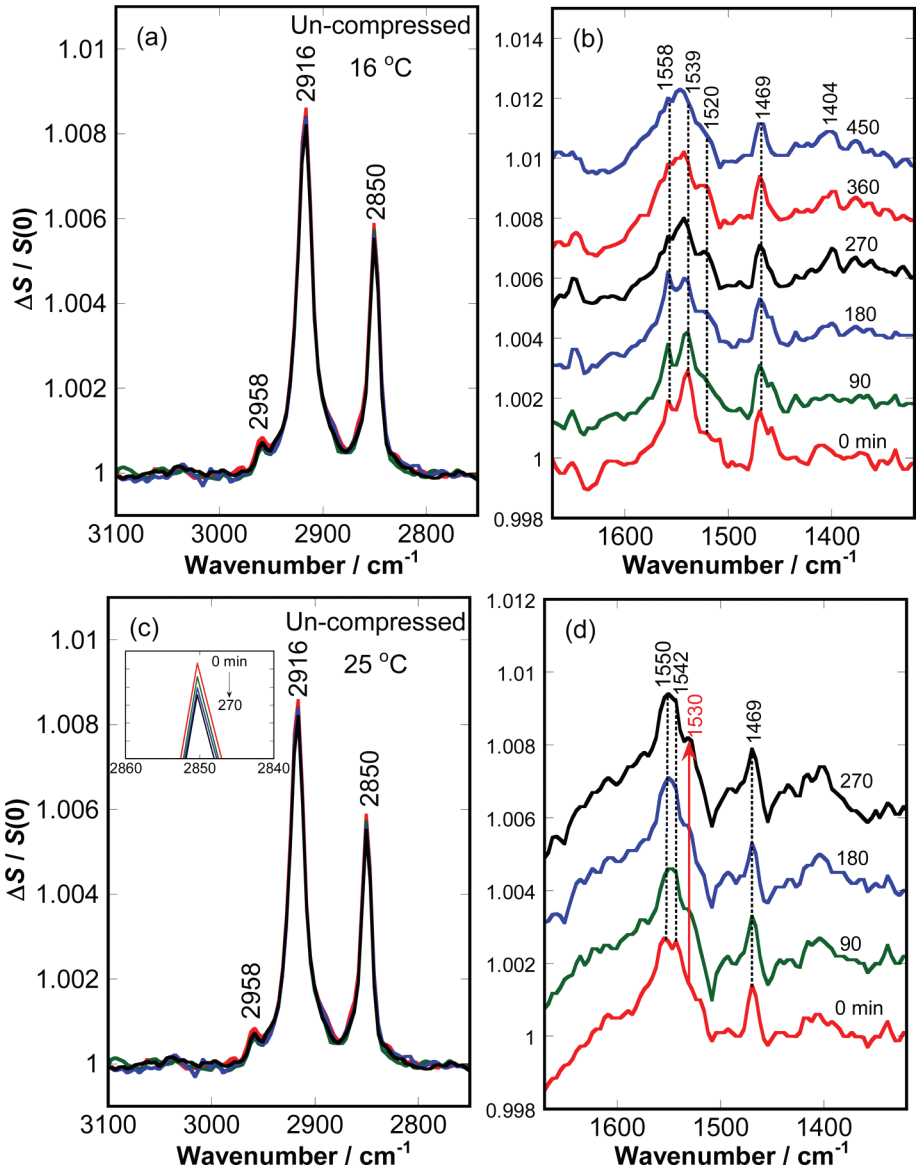


Figure 1. PM-IRRAS spectra of the 'uncompressed' L film of zinc stearate prepared at 16 °C ((a) and (b)) and measured at 25 °C (c) and (d).

are known to be arranged in a parallel manner (Type II in Scheme 1) due to the crystal packing.[29] When the crystallite is hydrated, however, water molecules play a role of regulating intermolecular spacing, which causes the symmetric coordination structure about a cation[30] (Type III in Scheme 1). This can be done when the molecular uniformity near the water surface is imperfect due to the uncompression technique. In the present case, the L film is directly on water and the coordination part can involve water molecules. The symmetric coordination structure should be more preferable with respect to localized molecular vibration. Type III has thus been assigned to the band at 1520 cm^{-1}. In short, the nonuniformed structure disappears while uniformed structure having the symmetric coordination develops at 16 °C.

Similar experiments were performed at 25 °C as presented in parts c and d of Figure 1. At this temperature, Type I band appears at 1550 cm^{-1} and Type II band is at 1542 cm^{-1}, whose interval is less than that at 16 °C. The lower wavenumber shift of Type I band suggests that Type I species at 25 °C has a better organized structure than that at 16 °C because of the temperature-induced molecular mobility. Type III band develops at 1530 cm^{-1} with time as indicated by the red arrow in part d of Figure 1, which suggests that the bidentate coordination through the molecular reorientation occurs. Regardless, the coordination structure about the cation at 25 °C may be different from that at 16 °C because the band position is shifted. This change of coordination structure should accompany a change of molecular tilting, which should be reflected in the C−H stretching vibration bands.

The C−H stretching vibration region of the same L films measured at 16 and 25 °C are presented in parts a and c respectively of Figure 1. The difference at the two temperatures is found in the change of the band intensity. The intensity change is ignorable within an experimental error at 16 °C, whereas the change at 25 °C monotonously appears: both the antisymmetric and symmetric C−H stretching vibration bands simultaneously decrease in intensity with time as shown in the insert of part c of Figure 1. Judging from the surface selection rule, the decreasing changes indicate that the molecules are ordered at an initial stage, but the ordered structure is getting

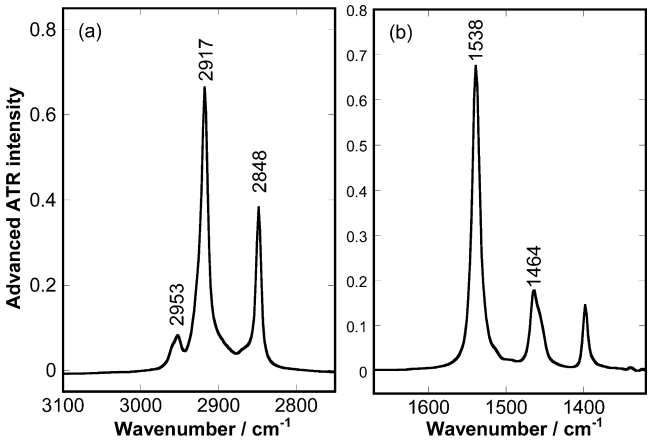


Figure 2. Infrared ATR spectra of collapsed L films of zinc stearate. The spectra are converted to be absorptivity spectra, so that the band positions can directly be compared to those in ordinary transmission and PM-IRRAS spectra.

slightly tilted with time. This very minor but systematic orientation change should be induced by the structural change about the zinc cation.

If the coordination structure about a zinc cation changes with time, the change in the chemical atmosphere about the cation should be monitored by polarized XANES spectra,[31] which is sensitive to the electronic distribution structure about a metal ion. The time-dependent XANES spectra of an uncompressed L film of stearic acid on a zinc bromide solution are presented in Figure 3. The s-polarized spectrum of the fresh film

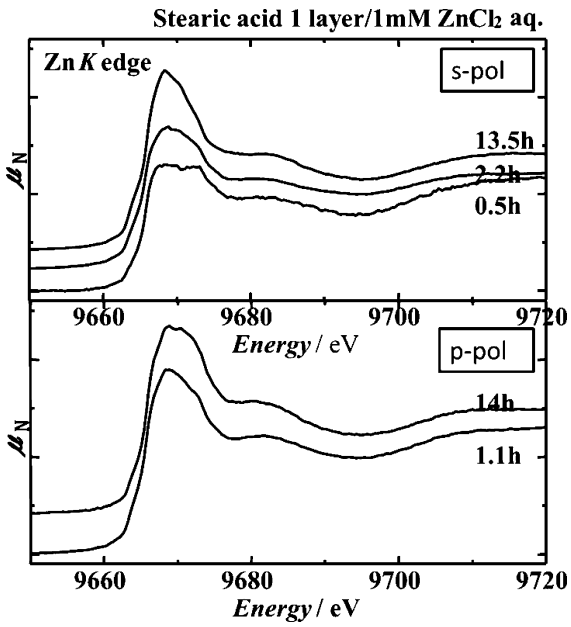


Figure 3. Polarized XANES spectra of the uncompressed L film of zinc stearate prepared at 16 °C.

exhibits doublet peaks near the absorption edge, but the peak at 9672 eV can be excluded from the discussion because only the height of the white line is necessary.[15] After 13 hours, the white line intensity increases, which indicates that the coordination number increases from four to five evaluated by using an established analytical technique.[14]

Because the identical L film is measured by s- and p-polarizations sequentially in turn, each of which takes 30 minutes, the initial stage of the L film was observed only by s-polarization. Therefore, only minute change is recognized in the p-polarization spectra. In other words, a significant change finishes in an early stage only in about thirty minutes.

To discuss the time-dependent s-polarized XANES spectra, the orientation of the $-COO^-$ group should be known. Fortunately, we find another important fact of the PM-IRRAS spectra in Figure 1: the integral intensity of the $\nu_s(COO^-)$ vibration band at 1404 cm^{-1} is much weaker than that of the $\nu_a(COO^-)$ vibration band in the PM-IRRAS spectra with respect to the ATR spectrum in Figure 2. Because the ATR spectrum reflects the isotropic molecular arrangement, the change of the relative band intensity appeared in the PM-IRRAS spectra suggests that the $-COO^-$ group is oriented in the L film. Judging from the surface selection rule of PM-IRRAS (Experimental section), the decrease of the $\nu_s(COO^-)$ vibration band indicates that the line connecting through the two oxygen atoms of the $-COO^-$ group is aligned nearly parallel to the film surface, whereas the bisector of the $-COO^-$ group should be tilted to the film surface as illustrated in Figure 4. Note that only the red-marked portions contribute to the coordination.

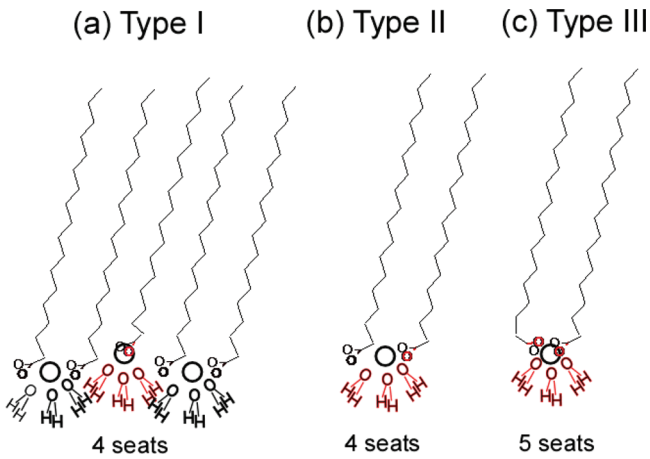


Figure 4. Schematics of the coordination structure about a zinc cation surrounded by water and stearic acid molecules. The portions marked by red contribute to the coordination.

As stated in the paper of Watanabe's group, XANES and EXAFS spectral regions both indicate that zinc cation in the L film surface has a tetracoordinate structure at an initial stage, and it gradually changes to a pentacoordinate structure. In the present study, the XANES spectral variation reproduces the previous results. Because the cation has the hexacoordinated octahedral structure when it is fully hydrated in an aqueous solution, the tetra- and pentacoordinated structures are both characteristic structures in the L film surface. An XAFS spectrum is, however, a result of a linear combination of pieces of spectral information. Therefore, an XAFS spectrum cannot deny a possibility that the pentacoordinated structure may be an average of tetracoordinate and hexacoordinate structures. In the present study, very fortunately, the PM-IRRAS spectra have revealed that the coordination structure changes from Type II to Type III, which takes a very long period of time though. Because this change corresponds to an increase of coordination by one, the pentacoordinated structure has readily been

confirmed experimentally. Here, note that only one atom can coordinate with the zinc cation through the $d-\pi^*$ interaction because it is limited by the d-orbital shape of the cation, although a carboxyl group has two oxygen atoms.

Because the white-line analysis responds to the change of coordination structure, XAFS cannot discuss the change from Type I to Type II. This is a reason the XAFS spectral changes do not synchronously correspond to the changes of the PM-IRRAS spectra.

Compressed L Film. When an L film is prepared by the Langmuir technique employing a compression bar, however, the molecules in the L film are expected to aggregate in a more ordered manner than the uncompressed film. The key of the compressed L film is that the molecular arrangement is determined when the monolayer compression has been finished because the slow compression of the L film is considered to be a continuous reversible equilibrium process.

To examine this expectation, time-dependent XAFS spectra of the compressed L film up to 15 mN m^{-1} were measured, which are presented in Figure 5. During the measurements, the

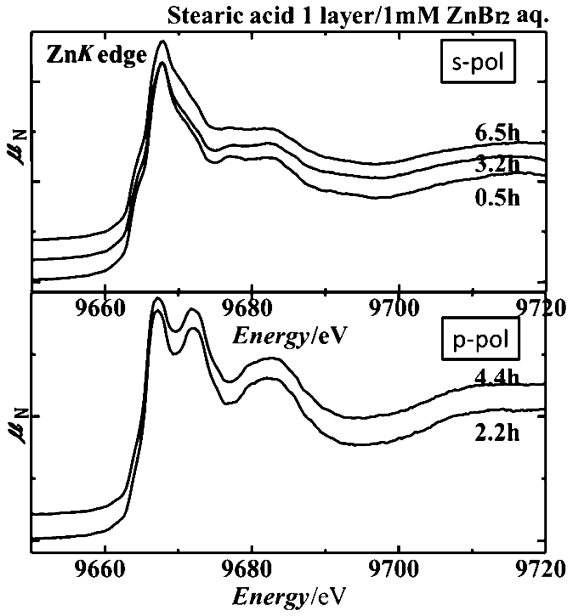


Figure 5. Polarized XANES spectra of the 'compressed' L film of zinc stearate at 20 mN m^{-1} and 16 °C.

surface area of the L film was kept unchanged even at an early stage of the s-polarization measurements. The white line intensity of the s-polarization XANES spectra indicates that the coordination number is five,[15,16] which suggests that the pentacoordinate structure occupies the major portion at the monolayer surface.

PM-IRRAS spectra of a compressed L film with time are presented in Figure 6. Both the C−H stretching vibration and the fingerprint regions exhibit ignorable band-intensity changes within an experimental error over eight hours, which is consistent with the XAFS results. In particular, the change of the C−H stretching vibration is quite minor in comparison to that found in Figure 1. Therefore, the compressed film proves to have a highly ordered and uniformed structure limitedly in the hydrocarbon chains. Nonetheless, Type III band that corresponds to the pentacoordinate structure does not develop significantly. This discrepancy between the IR and XAFS results

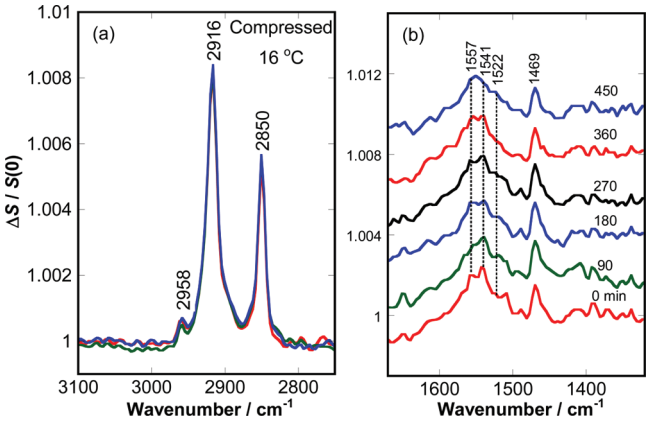


Figure 6. PM-IRRAS spectra of the compressed L film of zinc stearate at 20 mN m^{-1} and 16 °C.

may be because another water molecule participates in coordination with a zinc cation. Since the compressed L film has a highly uniformed structure, another water molecule can be involved in the coordination in place of the uncoordinated stearic acid.

To have a higher mobility of molecules in the compressed L film to rearrange the carboxylic group, PM-IRRAS measurements were also performed at 25 °C. The spectra are presented in Figure 7. Regardless, the results are almost the same as those

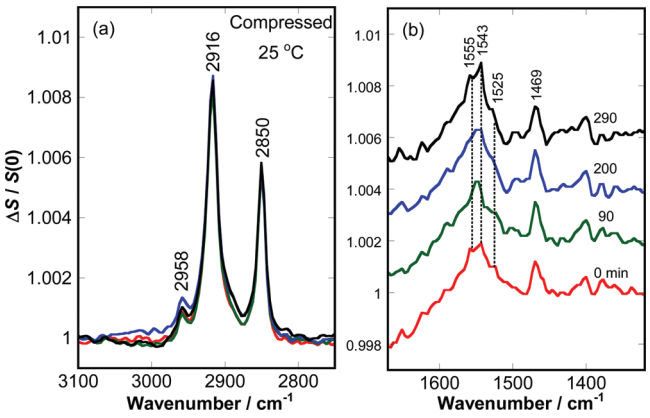


Figure 7. PM-IRRAS spectra of the compressed L film of zinc stearate at 20 mN m^{-1} and 25 °C.

in Figure 6, and no development of Type III was reconfirmed. This supports that the highly uniformed structure throughout the L film plays a dominant role in keeping the asymmetric headgroup arrangement, which is unfavorable to coordination with a zinc cation.

■ CONCLUSIONS

A Langmuir film of zinc stearate has been analyzed by using IR and X-ray absorption spectra to illustrate dynamic molecular arrangement in the cross section image as a function of the film preparation method: compression and uncompression techniques. Through the spectroscopic analysis, the compressed L film has been found to attain a stable state where the molecular arrangement is fixed at an early stage; whereas the uncompressed film takes a long period of time for attaining a stable state, but it can attain a higher ordered coordination structure about the headgroup than the compressed one. Thus far, the

compression technique has long been believed to be necessary to have a highly uniformed aggregation structure in an L film, but this has been revealed to be true only when the coordination structure about a metal cation is excluded from discussion.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by Grant-in-Aid for Scientific Research (B) (No. 23350031(TH) and 21350047(MH)), and Priority Areas (No. 23106710) from the Ministry of Education, Science, Sports, Culture, and Technology, Japan. The synchrotron radiation experiments were performed at BL39XU of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2010A1448).

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