Colloid Polym Sci (2008) 286:1637–1641
DOI 10.1007/s00396-008-1939-2

ORIGINAL CONTRIBUTION

Evaluation of structural change during surface pressure relaxation in Langmuir monolayer of zinc stearate by infrared external reflection spectroscopy

Hiroshi Sakai · Junzo Umemura

Received: 25 August 2008 / Revised: 26 September 2008 / Accepted: 30 September 2008 / Published online: 14 October 2008

Abstract In situ polarized infrared external reflection spectra of the Langmuir monolayer of zinc stearate on a water surface were recorded during surface pressure relaxation, and the molecular structure of the monolayer was evaluated. The wavenumber of the antisymmetric methylene stretching band decreased during surface pressure relaxation. This result indicated that the shift to a highly compact packing of the hydrocarbon chain in the Langmuir monolayer occurred on a time scale of several minutes. Moreover, a wavenumber change in the antisymmetric carboxylate stretching band was observed. The O–C–O angle of the carboxylate group and the binding nature of the zinc cation to the carboxylate group appeared to have changed during the relaxation. The orientation angle of the molecule and the time scale of relaxation mechanisms were also discussed.

Keywords Langmuir monolayer · Surface pressure relaxation · Infrared spectroscopy · External reflection spectroscopy · Zinc stearate · Relaxation time

H. Sakai (✉)
Heian Jogakuin (Saint Agnes') University,
Nampeidai, Takatsuki,
Osaka-Fu 569-1092, Japan
e-mail: sakai@heian.ac.jp

J. Umemura
Ikeyama, Todou, Uji,
Kyoto-Fu, 611-0013, Japan

Introduction

When a Langmuir monolayer on a water surface is compressed and held to a certain surface area, the surface pressure of the Langmuir monolayer decreases. This temporal phenomenon is called surface pressure relaxation. The relaxation is due to the viscoelasticity of the monolayer and is therefore a dynamic phenomenon. The elucidation of the relaxation mechanisms is important for understanding not only molecular interactions occurring in the system but also the stability of the Langmuir monolayer, which is an essential parameter in thin film technology [1, 2].

Various studies have been conducted on surface pressure relaxation [3–13], and some mechanisms have been presumed, such as the collapse of the monolayer into a three-dimensional state, dissolution into the bulk phase, etc. In many studies on dynamic phenomena in Langmuir monolayers, including the study on surface-area changes occurring at constant surface pressure [14–20], macroscopic measurement or Brewster angle microscopy was frequently used. However, limited work has been carried out on the spectral study of the molecular behavior. In addition, the Langmuir monolayer is susceptible to metal ions in the subphase [21–23]. Certain kinds of metal ions lead to the condensation of π–A isotherms of fatty acid monolayers. The molecular configuration in Langmuir monolayers with metal ions has attracted considerable attention because of their many potential applications. However, studies on the role of metal ions at the molecular level during surface pressure relaxation are still lacking.

In the present study, in situ polarized infrared external reflection (IER) spectra of the Langmuir monolayer of zinc stearate were recorded during surface pressure relaxation, and the molecular structure of the monolayer was evaluated. Infrared spectroscopy has the advantages of being easy to

use, nondestructive against samples, and sensitive to changes in the molecular configuration. There have already been many investigations of Langmuir monolayers by IER spectroscopy under various conditions [9, 11, 24–37]. However, only limited work has been conducted under the dynamic conditions. In previous studies [9, 11], we have measured the IER spectra of the Langmuir monolayers of stearic acid and 12-hydroxystearic acid during surface pressure relaxation and have elucidated that the relaxation is due to the collapse of the monolayer based on observing of the methylene stretching band. We have also investigated the zinc stearate monolayer with various surface areas during stepwise compression and have elucidated specific features of the zinc ion [36]. Thus, this study is conducted by employing IER spectroscopy for evaluating structural changes occurring at the molecular level in the Langmuir monolayer of zinc stearate during surface pressure relaxation. In addition, we discuss the relaxation time corresponding to each relaxation mechanism by curve fitting analysis.

Experimental

Stearic acid was the same as previously reported [26]. All other reagents were either of high purity (above 98%) or of spectroscopic grade. Water was prepared by an IWAKI GLASS, Model ASK-2DS auto still and a Millipore Simpli Lab system.

The Langmuir monolayer of zinc stearate was prepared on an aqueous solution of 1×10^{-3} M $ZnCl_2$ by spreading 11.3 μL of an 8.12×10^{-4} M chloroform solution of stearic acid. A trough with an 80×22 mm^2 effective surface area attached to a Specac 19650 monolayer/grazing angle accessory was used. An S. T. Japan Model STJ-100 wire-grid polarizer with 1,300 lines/mm Al wires on KRS-5 was placed just above the water surface to optimize the polarization. The IER spectra of the Langmuir monolayer were recorded using a Nicolet Nexus 460 FT-IR spectrophotometer equipped with a deuterated triglyceride sulfate detector with a resolution of 8 cm^{-1}. The incident angle was 42° using an s-polarized beam.

First, the background spectrum was collected with 1,500 scans at the aqueous solution surface, and then the solution of stearic acid was spread. After waiting for 10 min to allow the solvent to completely evaporate, the Langmuir monolayer was compressed at a constant velocity of 0.03 nm^2 per molecule per minute down to a surface area of 0.20 nm^2 per molecule, which is typical of the solid-phase region [36]. Immediately after compression, 30 IER spectra of 100 scans each were successively recorded.

The surface-pressure relaxation isotherm was measured by a Wilhelmy balance attached to a USI, Model FSD-220 Film Balance Controller. The compression velocity of the Langmuir monolayer was 0.03 nm^2 per molecule per minute. All experiments were performed at 25 °C.

Results and discussion

The surface-pressure relaxation isotherm of the Langmuir monolayer of zinc stearate compressed to a surface area of 0.20 nm^2 per molecule is shown in Fig. 1. Initially, the pressure significantly decreases, and then, the decrease becomes more gradual. At first glance, the rate at which surface pressure of zinc stearate appears to attain equilibrium is considerably slower than that of stearic acid [9]. Zinc cations may induce a high viscosity in the Langmuir monolayer.

Figure 2 shows the IER spectra of the Langmuir monolayers of zinc stearate between 3,500 and 1,000 cm^{-1} under various elapsed times after compression. In this frequency region, the antisymmetric and symmetric methylene stretching bands (ν_aCH_2 and ν_sCH_2) at about 2,914 and 2,850 cm^{-1}, respectively, the antisymmetric and symmetric carboxylate stretching bands (ν_aCOO^- and ν_sCOO^-) at about 1,542 and 1,398 cm^{-1}, respectively, the methylene scissoring band (δ CH_2) at about 1,473 cm^{-1}, and the band of water at about 1,660 cm^{-1} are observed. In the external reflection measurements of the Langmuir monolayers on the water surface, the reflection absorbances appear positive or negative (upward or downward) depending on the direction of the transition moment, the angle of incidence, and the polarization of the incident beam [25]. Under the present condition (s-polarization), the observed infrared bands of the monolayer show negative reflection absorbances, while the bands of water show a positive reflection absorbance [34].

It is known that the wavenumber of the ν_aCH_2 band is sensitive to molecular conformation and packing [26, 38].

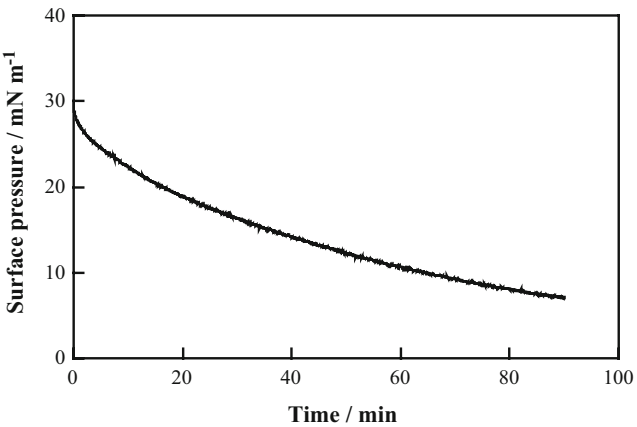

Fig. 1 Surface-pressure relaxation isotherm of Langmuir monolayer of zinc stearate compressed to a surface area of 0.20 nm^2 per molecule

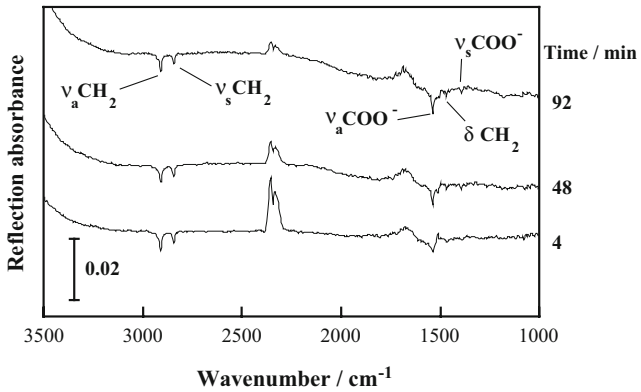

Fig. 2 IER spectra of Langmuir monolayers of zinc stearate measured by an s-polarized beam at 4, 48, and 92 min after compression

In a previous study [9], we have concluded that the relaxation mechanism of the Langmuir monolayer of stearic acid is the collapse based on observing the increase in the wavenumber of the band. The wavenumber of the ν_aCH_2 band of the zinc stearate monolayer versus time after compression is shown in Fig. 3. Interestingly, the trend of the change in the wavenumber of zinc stearate was exactly opposite to that of stearic acid. The wavenumber of stearic acid increased from about 2,917 cm^{-1} to about 2,918 cm^{-1} during relaxation [9]. In contrast, the wavenumber of zinc stearate decreased from about 2,916.5 cm^{-1} to about 2,914.5 cm^{-1}. The increase in the wavenumber of stearic acid indicates an increase in the gauche conformation or a chain disorder. Some molecules in the compressed monolayer slip out upward to form molecules with a disordered chain by acquiring free space. In zinc stearate, the shift to the highly compact packing of the hydrocarbon chain is evaluated. The result of this evaluation resembles crystal growth of polymers under strain [39]. It is possible that the packing density increases with elapsed time due to the zinc atom in the Langmuir monolayer. Since the zinc atom has a relatively small ionic or covalent radius among various divalent cations [40, 41], the condensation effect is strong [42]. Upon compression, on the other hand, the wavenumber of zinc stearate for Langmuir monolayer having various areas did not change at around 2,914 cm^{-1} [36]. In that measurement, the process carried out was stepwise such that the IER spectrum was recorded after compressing a certain amount of the surface area; this process was repeated many times. Relaxation probably occurred within a short range in that case.

Figure 4 shows the peak intensities (absolute values) of the ν_aCH_2 and ν_sCH_2 bands versus time after compression. The peak intensities of both bands decrease with elapsed time. The result shows that the transition moments of both bands show a trend of being perpendicular to the water surface, and the orientation angle of the hydrocarbon chain increases from the surface normal; i.e., the chain tilts [33]. It is possible that the hydrocarbon chain initially stands almost perpendicular to the water surface just after compression. The increase in the orientation angle can be attributed to crystal growth in two or three dimensions during relaxation; the hydrocarbon chain tilts until the crystal attains an equilibrium state.

Figure 5 shows the wavenumber of the ν_aCOO^- band versus time after compression. Initially, the wavenumber increased from about 1,540.5 cm^{-1} to about 1,543 cm^{-1}, and then, the wavenumber remained almost constant. As discussed in a previous paper [36], the ν_aCOO^- wavenumber depends on the O–C–O angle, α, of the carboxylate group as follows [43]:

$$\nu_a COO^- = 1,303\sqrt{K\left(\frac{1}{m_o}+\frac{1-\cos\alpha}{m_c}\right)} \quad (1)$$

where K is the C–O stretching force constant in millidynes per angstrom, and m_o and m_c are the relative atomic masses

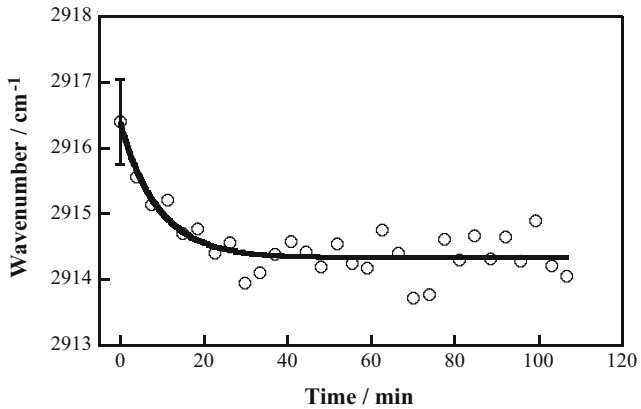

Fig. 3 Wavenumbers of ν_aCH_2 band in Langmuir monolayer of zinc stearate vs. elapsed time after compression. The result of curve fitting is shown by the *solid line*. The *error bar* is estimated from observed band shape distortions and noise level in the background region

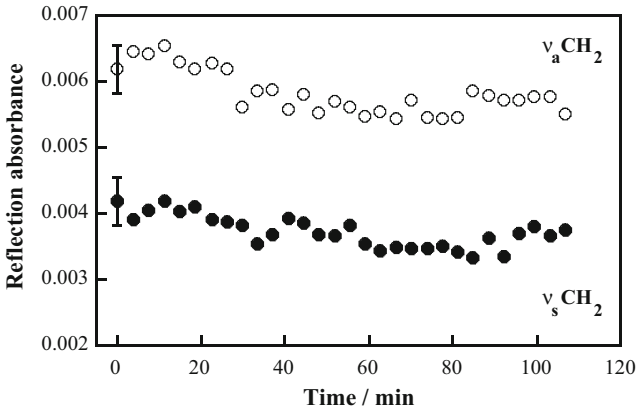

Fig. 4 Peak intensities of ν_aCH_2 (*open circle*) and ν_sCH_2 (*solid circle*) bands in Langmuir monolayer of zinc stearate vs. elapsed time after compression. The *error bar* is estimated from the noise level in the background region

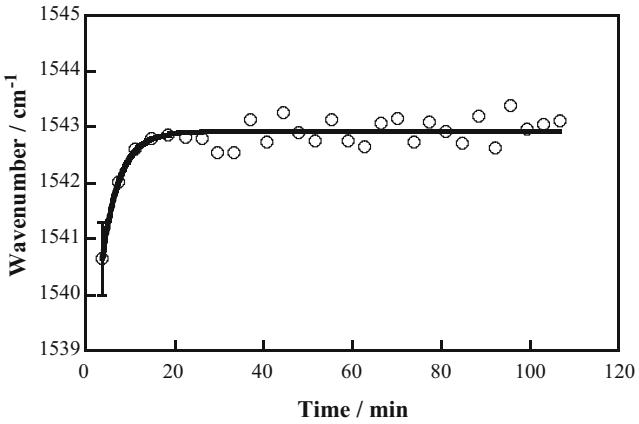

Fig. 5 Wavenumbers of ν_aCOO^- band in the Langmuir monolayer of zinc stearate vs. elapsed time after compression. The result of curve fitting is shown by the *solid line*. The *error bar* is estimated from observed band shape distortions and noise level in the background region

of oxygen and carbon, respectively. Substitutions of K=7.2 [44], m_c=12.01, m_o=16.00, and the previous ν_aCOO^- wavenumbers into Eq. 1 cause an increase in the value of α from 125.5° to 126.1° during relaxation. In addition, metal cations can bind to the carboxylate group in several ways [45]. In a previous paper [36], we assigned zinc stearate to the bidentate structure in the monolayer. The wavenumber change in this study may be assigned either to the chelating-bridging bidentate structural change or to the coordination number change [46].

Figure 6 shows the peak intensities of the ν_aCOO^- and ν_sCOO^- bands versus time after compression. The peak intensities of both bands increase with elapsed time. This result shows that the transition moments of both bands show a trend of being parallel to the water surface. Thus, the O–C–O plane becomes parallel to the water surface

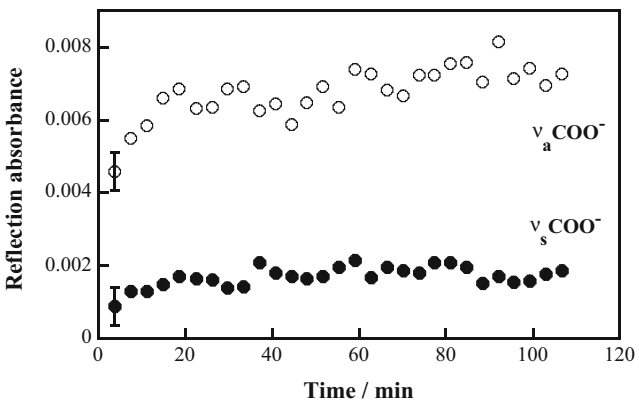

Fig. 6 Peak intensities of ν_aCOO^- (*open circle*) and ν_sCOO^- (*solid circle*) bands in Langmuir monolayer of zinc stearate vs. elapsed time after compression. The *error bar* is estimated from the noise level in the background region

during relaxation. The trend is quite consistent with the tilting of the hydrocarbon chain.

Finally, we discuss the time scale of the relaxation mechanism. The above-mentioned spectral changes of the methylene and the carboxylate groups do not appear to synchronize with the surface pressure change. For the analysis of the time scale in these changes during relaxation, curve fitting was carried out using the following exponential equation:

$$(w - w_e)/w_0 = a\ \exp(-t/\tau_1) \tag{2}$$

where w, w_0, and w_e are the wavenumbers at time t, 0, and at equilibrium, respectively; τ_1 is the relaxation time; and a is a pre-exponential factor. These results are shown in Figs. 3 and 5 by the solid line. The relaxation times τ_1 of the ν_aCH_2 band and ν_aCOO^- band were 9.1 (±2.2, standard error) and 3.9 (±0.9), respectively. However, the surface-pressure relaxation isotherm could not be fitted using Eq. 2. Therefore, we used another equation:

$$(\pi - \pi_e)/\pi_0 = a\ \exp(-t/\tau_1) + (1-a)\exp(-t/\tau_2) \tag{3}$$

where π, π_0, and π_e are the surface pressures at time t, 0, and at equilibrium, respectively, and τ_1 and τ_2 are the relaxation times, whose values were 2.2 and 68.9, respectively (the errors were negligible). These results suggest that two mechanisms occur during surface-pressure relaxation. The relaxation time τ_1 of the surface pressure probably corresponds to these molecular structural changes, and the relaxation time τ_2 corresponds to another mechanism. In this case, the latter mechanism is a mechanism other than the dissolution of molecules into the bulk phase due to the very low solubility. This can be attributed to the fact that the two-dimensional crystal converts to a three-dimensional one or the holes between domains in the Langmuir monolayer are gradually filled on the time scale of several tens of minutes. In conclusion, the pressure relaxation of the zinc stearate monolayer is subject to two mechanisms: one is the molecular structural changes on the time scale of several minutes, and the other is mesoscopic or macroscopic changes on the time scale of several tens of minutes.

Conclusion

We have investigated the Langmuir monolayer of zinc stearate on a water surface during surface pressure relaxation by polarized IER spectroscopy and evaluated the molecular structure of the monolayer. The wavenumber of the antisymmetric methylene stretching band decreases during surface pressure relaxation. This result implies that the shift to a highly compact packing of the hydrocarbon chain occurs due to the zinc atom in the Langmuir monolayer during relaxation. In addition, the orientation

angle of the hydrocarbon chain tilts from the surface normal during relaxation. Moreover, the wavenumber change of the antisymmetric carboxylate stretching band is observed. The result would suggest that the O–C–O angle of the carboxylate and the binding nature of the zinc cation to the carboxylate group change. In addition, a curve fitting analysis confirmed that pressure relaxation is subject to two mechanisms, each with a different time scale, i.e., several minutes and several tens of minutes. The change in the above-mentioned molecular structure corresponds to the former mechanism.

Acknowledgments This research was partially supported by KAKENHI (13554027) and (18700579).

References

1. Robert GG (ed) (1990) Langmuir-blodgett films. Plenum Press, New York
2. Ulman A (1991) An introduction to ultrathin organic films. Academic, Boston
3. Rabinovitch W, Robertson RF, Mason SG (1960) Can J Chem 38:1881
4. Gabrielli G, Guarini GGT, Ferroni E (1976) J Colloid Interface Sci 54:424
5. Tabak SA, Notter RH, Ultman JS (1977) J Colloid Interface Sci 60:117
6. Bois AG, Baret JF, Kulkarni VS, Panaiotov II, Ivanova MG (1988) Langmuir 4:1358
7. Adams J, Buske A, Duran RS (1993) Macromolecules 26:2871
8. Wang L-F, Kuo J-F, Chen C-Y (1995) Colloid Polym Sci 273:426
9. Sakai H, Umemura J (1996) Chem Lett 465
10. Ganguly P, Paranjape DV, Patil KR, Sastry M, Rondelez F (1997) Langmuir 13:5440
11. Sakai H, Umemura J (1998) Langmuir 14:6249
12. Viseu MI, Goncalves da Silva AM, Costa SMB (2001) Langmuir 17:1529
13. Wojciechowski K, Grigoriev D, Ferdani R, Gokel GW (2006) Langmuir 22:8409
14. Neuman RD (1976) J Colloid Interface Sci 56:505
15. Smith RD, Berg JC (1980) J Colloid Interface Sci 74:273
16. Vollhardt D, Retter U (1991) J Phys Chem 95:3723
17. Vollhardt D, Retter U, Siegel S (1991) Thin Solid Films 199:189
18. Vollhardt D, Retter U (1992) Langmuir 8:309
19. Wang LF, Kuo JF, Chen CY (1995) Mater Chem Phys 40:197
20. Broniatowski M, Vila-Romeu N, Nieto-Suarez M, Dynarowicz-Łątka P (2007) J Phys Chem B 111:12787
21. Gaines GL Jr (1966) Insoluble monolayers at liquid-gas interfaces. Interscience Publishers, New York
22. Yazdanian M, Yu H, Zografi G (1990) Langmuir 6:1093
23. Binks BP (1991) Adv Colloid Interface Sci 34:343
24. Dluhy RA, Cornell DG (1985) J Phys Chem 89:3195
25. Dluhy RA (1986) J Phys Chem 90:1373
26. Sakai H, Umemura J (1993) Chem Lett 2167
27. Gericke A, Hünerfuss H (1993) J Phys Chem 97:12899
28. Buontempo JT, Rice SA (1993) J Chem Phys 98:5825
29. Blaudez D, Buffeteau T, Cornut JC, Desbat B, Escafre N, Pezolet M, Turlet JM (1993) Appl Spectrosc 47:869
30. Flach CR, Brauner JW, Mendelsohn R (1994) Biophys J 65:1994
31. Ren Y, Meuse CW, Hsu SL, Stidham HD (1994) J Phys Chem 98:8424
32. Sakai H, Umemura J (1997) Langmuir 13:502
33. Sakai H, Umemura J (1997) Bull Chem Soc Jpn 70:1027
34. Umemura J, Sakai H (1999) In: Itoh K, Tasumi M (eds) Fourier Transform Spectroscopy Twelfth International Conference, 127
35. Urai Y, Ohe C, Itoh K, Yoshida M, Iimura K, Kato T (2000) Langmuir 16:3920
36. Sakai H, Umemura J (2002) Colloid Polym Sci 280:316
37. Wang C, Zheng J, Zhao L, Rastogi VK, Shah SS, DeFrank JJ, Leblanc RM (2008) J Phys Chem B 112:5250
38. Kawai T, Umemura J, Takenaka T, Kodama M, Seki S (1985) J Colloid Interface Sci 103:56
39. Gotoh R, Takenaka T, Umemura J, Hayashi S (1966) Bull Inst Kyoto Univ 44:286
40. Rajagopal A, Kulkarni SK, Dhanabalan A, Major SS (1998) Appl Surf Sci 125:178
41. Pauling L (1960) The nature of the chemical bonds, 3rd edn. Cornell University Press, New York
42. Tano T, Umemura J (1997) Langmuir 13:5718
43. Colthup NB, Daly LH, Wiberley SE (1990) Introduction to infrared and raman spectroscopy, 3rd edn. Academic, New York, p 192
44. Grigor'ev AI (1963) J Inorg Chem 8:409
45. Nakamoto K (1997) Infrared and Raman spectra of inorganic and coordination compounds, 5th edn. Wiley, New York
46. Watanabe I, Tanida H, Kawauchi S (1997) J Am Chem Soc 119:12018