Crystal lattice of the cadmium alkanoate monolayer at the air/water interface investigated by polarization modulation infrared spectroscopy

Yanzhi Ren, Ken-ichi Iimura, and Teiji Kato

Articles you may be interested in

Polarization and experimental configuration analyses of sum frequency generation vibrational spectra, structure, and orientational motion of the air/water interface
J. Chem. Phys. **124**, 114705 (2006); 10.1063/1.2179794

Surface phase behavior in Langmuir monolayers of diethylene glycol mono- n -hexadecyl ether at the air-water interface
J. Chem. Phys. **121**, 10217 (2004); 10.1063/1.1806818

Second-harmonic generation and Maxwell displacement current spectroscopy of chiral organic monolayers at the air–water interface
J. Chem. Phys. **119**, 7427 (2003); 10.1063/1.1605943

Photoelastic modulation-reflection absorption infrared spectroscopy of CO on Pd(111)
J. Vac. Sci. Technol. A **20**, 2101 (2002); 10.1116/1.1517995

Crystal lattice transition of behenic acid monolayer on pure water surface observed by polarization modulation infrared spectroscopy
J. Chem. Phys. **114**, 6502 (2001); 10.1063/1.1366317

COMMUNICATIONS

Crystal lattice of the cadmium alkanoate monolayer at the air/water interface investigated by polarization modulation infrared spectroscopy

Yanzhi Ren, Ken-ichi Iimura, and Teiji Kato[a)]
Satellite Venture Business Laboratory, Utsunomiya University, Yoto 7-1-2, Utsunomiya, 321-8585, Japan

The crystal lattice of an arachidic acid/Cd^{2+} (CdA) monolayer on the surface of aqueous $CdCl_2$ subphase in a Langmuir trough was investigated *in situ* by polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). The spectra reveal a hexagonal packing of the hydrocarbon chains on the subphase of $pH=6.2$ and 293–283 K. Cooling from 283 to 280 K induces the hexagonal unit cell to transform to an orthorhombic one, as evidenced by the splitting of the CH_2 scissoring mode. This transition is observed to be reversible with temperature variation within 293–274 K. On the subphase of $pH=8.4$, the crystal lattice of CdA is orthorhombic even at 293 K. The temperature-dependent crystal lattice transition of CdA is compared with the monotonic hexagonal subcell of a cadmium stearate monolayer within 293–274 K and the orthorhombic subcell of a cadmium behenate monolayer within 293–274 K. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1342862]

The crystal structure of lipid monolayers floating at the air/water interface is of broad interest to the scientific community.[1–3] The technique to make such monolayers involves dissolving an amphiphile into an evaporative solvent and then spreading it onto the water surface. Among all the lipid monolayers, the arachidic acid/Cd^{2+} (CdA) system on the aqueous $CdCl_2$ subphase is deemed to be the best understood. The following information, derived from synchrotron x-ray studies, is all we know about the crystal lattice of floating CdA monolayers. At ($0.28 \, nm^2$, 293 K, $pH=6.7$) CdA has a hexagonal unit cell that contains only one crystallographically independent hydrocarbon chain, the long axis of the *trans* zig–zag chain being perpendicular to the water surface.[4,5] At ($0.28 \, nm^2$, 282 K, $pH=8.8$) CdA has a pseudo-orthorhombic unit cell that contains two crystallographically independent hydrocarbon chains, the chain axis being tilted at 11° with respect to the surface normal.[6]

The above two data are about spontaneously formed CdA monolayers after spreading to the aqueous Cd^{2+} subphase. In this communication we shall do two experiments. The first is to compress the spontaneously formed monolayer and observe the crystal lattice change. The action of compressing lipid monolayers on the water surface by movable barriers is usually desired in the Langmuir–Blodgett technique. The second is to vary the subphase temperature and observe the crystal lattice change. This action is desirable from the viewpoint of membrane-mimetic chemistry.

We shall apply the newly developed technique, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS),[7] to obtain an *in situ* picture of the crystal lattice of lipids floating on water surface. A Langmuir trough

with excellent temperature-regulation ability is dedicated to this purpose. The PM-IRRAS spectra were recorded at $4 \, cm^{-1}$ and 300 scans using the Nicolet Magna 860 FTIR spectrometer. The spectra were reported as $-S(d)/S(o)$, where d and o stand for the monolayer-covered and uncovered subphase, respectively.[7]

The CH_2 scissoring vibration mode $\delta(CH_2)$ will be used as a fingerprint of the crystal lattice of hydrocarbon chains.[8,9] A broad singlet $\delta(CH_2)$ band at $1469-1467 \, cm^{-1}$ is indicative of a hexagonal unit cell. Figure 1 shows the PM-IRRAS spectra of CdA monolayers on the subphase of $pH=6.2$ around room temperature. The total deprotonation of arachidic acid at this pH has already been proposed by Simon-Kutscher *et al.*[8] We manually collected the collapsed CdA films from the subphase and measured the standard transmission spectrum. No band appears in the region $1800-1700 \, cm^{-1}$ corresponding to either free or hydrogen-bonded $\nu(C{=}O)$ modes. It is seen from Figs. 1(a) to 1(e) that the hydrocarbon chains in the CdA monolayers possess a hexagonal packing at the points ''a'' to ''e'' along the surface pressure-area (π–A) isotherm. This result implies that the crystal lattice at $pH=6.2$ is independent of the compressing state of the monolayer. The compression is stepwise, since the moving barrier has to stop during the PM-IRRAS measurement. The barrier stop causes the surface pressure to relax to some extent and the π-A isotherm is then discontinuous.

The spectra in Fig. 2 were recorded by holding the monolayer in a tight state (~ 21 mN/m, $0.210 \, nm^2$) and varying the subphase temperature. Figure 2(d) was recorded for the CdA monolayer with an experience of 280 K for 40 min. It is seen that the $\delta(CH_2)$ mode splits into two bands of equal intensities at 1473 and $1465 \, cm^{-1}$. This splitting is well known as representing an orthorhombic unit cell that
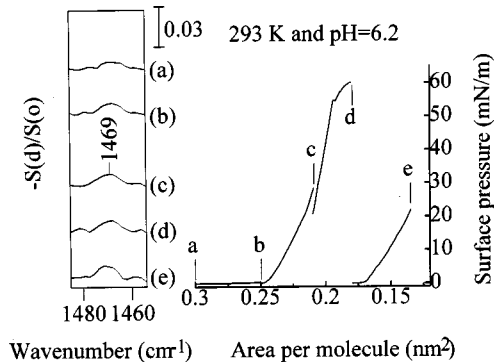
FIG. 1. PM-IRRAS spectra (left) and the corresponding surface pressure–area isotherm (right) of cadmium arachidate monolayers on the aqueous $CdCl_2$ subphase at 293 K. The subphase has a Cd^{2+} concentration of 5×10^{-4} M and a self-buffered pH of 6.2.

TABLE I. Crystal lattice of cadmium alkanoate in compressed monolayers on the aqueous Cd^{2+} subphase of concentration 5×10^{-4} M and pH $= 6.7-6.2$.

Temperature	Cd stearate	Cd arachidate	Cd behenate
293–283 K	hexagonal	hexagonal	orthorhombic
280–274 K	hexagonal	orthorhombic	orthorhombic

contains two crystallographically independent hydrocarbon chains. The CH_2 scissoring vibration of one chain can occur either in-phase or out-of-phase with respect to that of another chain, giving rise to the splitting. The extinction coefficients of the in-phase and out-of-phase $\delta(CH_2)$ modes are approximately equal for an orthorhombic unit cell.[10] As illustrated in the right chart of Fig. 2, the two nearest C–C–C planes have a dihedral angle of 90°. This chart is a simplified version of that depicted in Fig. 1 of Ref. 11. The hydrocarbon chain axis is perpendicular to the ab plane, i.e., the subphase surface. In addition, the CH_2 asymmetric and symmetric stretching bands are found respectively at 2916 and 2850 cm^{-1} in all the spectra presented in this communication (not shown). Such methylene stretching frequencies are known as representing a planar $trans$ zig–zag conformation of the hydrocarbon chain.[8]

In Fig. 2(f), where the CdA monolayer is experiencing 274 K, the $\delta(CH_2)$ mode splits into two bands, indicating an orthorhombic packing of the hydrocarbon chains. In Fig. 2(g), where the temperature has increased back to 283 K, the $\delta(CH_2)$ mode returns to a singlet band at 1467 cm^{-1}, indicating that the unit cell is again hexagonal. Therefore, the hexagonal-to-orthorhombic transition is reversible.

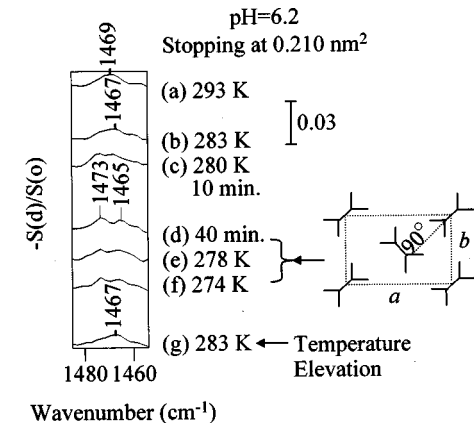We have also examined cadmium stearate (CdSt) and cadmium behenate (CdB) monolayers on the self-buffered aqueous Cd^{2+} subphase throughout the temperature range of 293–274 K.[12] Table I compares the crystal lattices of CdSt, CdA, and CdB in compressed monolayers. Behenic acid has two more CH_2 groups than arachidic acid, which in turn has two more CH_2 groups than stearic acid. It is seen that from room temperature down to the ice point, CdSt and CdB monolayers maintain to be hexagonal and orthorhombic, respectively.

The experiment in Fig. 3 was done for CdA monolayers on the Cd^{2+} subphase at 293 K and pH$= 8.4$. The monolayer collapses somewhere between the points ''c'' and ''d'' along the π-A isotherm. In Fig. 3(c) where the CdA monolayer is in the tightest state before collapse, the $\delta(CH_2)$ mode splits into two bands of equal intensities, implying an orthorhombic packing.

The orthorhombic packing of hydrocarbon chains is of wide interest to the scientific community. Using the atomic force microscope (AFM) it has been demonstrated that multilayers of CdA deposited on solid substrates can be orthorhombic, while a single monolayer of CdA can not be orthorhombic.[11] The present PM-IRRAS technique does reveal that floating CdA monolayers on the Cd^{2+} subphase can possess an orthorhombic unit cell, if choosing an appropriate pH. From our spectra in the COO stretching region as well as from other scientists' studies, it is known that the subphase Cd interacts ionically and covalently with the arachidate monolayer at pH of 8.4 and 6.2, respectively. At pH $= 8.4$ the interaction is via–$COO^-Cd^{2+}OH^-$, as proposed by x-ray studies.[6] At pH$= 6.2$ a chelating bidentate coordination forms, as proposed by IRRAS.[13] It is concluded that the electrostatic adhesive force at the interface of the $CH_3(CH_2)_{18}COO^-$ monolayer and the counterionic

FIG. 2. Temperature-dependent PM-IRRAS spectra of the tight cadmium arachidate monolayer on the aqueous $CdCl_2$ subphase at 0.210 nm^2. The subphase has a Cd^{2+} concentration of 5×10^{-4} M and a self-buffered pH of 6.2. The right scheme illustrates the orthorhombic packing derived from spectra (d), (e), and (f).
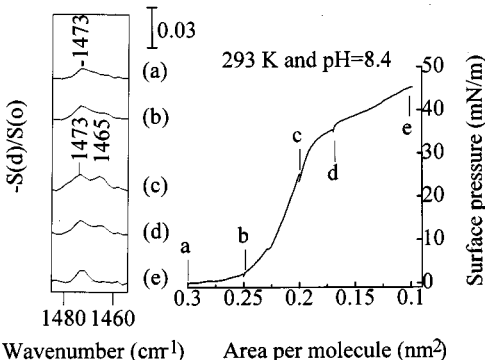

FIG. 3. PM-IRRAS spectra (left) and the corresponding surface pressure–area isotherm (right) of cadmium arachidate monolayers on the aqueous $CdCl_2$ subphase at 293 K. The subphase has a Cd^{2+} concentration of 5×10^{-4} M and a pH of pH$= 8.4$, adjusted with KOH.

$Cd^{2+}OH^-$ layer is responsible for the orthorhombic lattice on the subphase of pH$=8.4$.

Summarizing the experiments we have done, the appearance of an orthorhombic lattice in lipid monolayers depends on the lipid length, the surface pressure, the subphase temperature, and the adhesive interaction at the air/water interface. All these factors can be chosen to increase the constrain between adjacent hydrocarbon chains and thereby render an orthorhombic unit cell. A reversible hexagonal-to-orthorhombic transition of the famous CdA monolayer has been realized by varying the temperature of the self-buffered Cd^{2+} subphase.

[1] P. Dutta, J. B. Peng, B. Lin et al., Phys. Rev. Lett. **58**, 2228 (1987).

[2] M. J. Bedzyk, G. M. Bommarito, M. Caffrey, and T. L. Penner, Science **248**, 52 (1990).

[3] F. Leveiller, D. Jacquemain, M. Lahav et al., Science **252**, 1532 (1991).

[4] K. Kjaer, J. Als-Nielsen, C. A. Helm et al., J. Phys. Chem. **93**, 3200 (1989).

[5] P. Tippmann-Krayer, R. M. Kenn, and H. Möhwald, Thin Solid Films **210**, 577 (1992).

[6] F. Leveiller, C. Böhm, D. Jacquemain et al., Langmuir **10**, 819 (1994).

[7] D. Blaudez, J.-M. Turlet, J. Dufourcq et al., J. Chem. Soc., Faraday Trans. **92**, 525 (1996).

[8] J. Simon-Kutscher, A. Gericke, and H. Hühnerfuss, Langmuir **12**, 1027 (1996).

[9] J. G. Weers and D. R. Scheuing, in *Fourier Transform Infrared Spectroscopy in Colloid and Interface Science*, edited by D. R. Scheuing (American Chemical Society, Boston, 1991). Page 91 is about the $\delta(CH_2)$ mode of hexagonal (a singlet band around $1468\,cm^{-1}$) and orthorhombic packing (splitting to two bands) of hydrocarbon chains.

[10] R. G. Snyder, J. Mol. Spectrosc. **7**, 116 (1961).

[11] D. K. Schwartz, J. Garnaes, R. Viswanathan, and J. A. N. Zasadzinski, Science **257**, 508 (1992).

[12] We have reported the orthorhombic unit cell of a cadmium behenate monolayer at 293 K, identified by PM-IRRAS. Y. Z. Ren, M. Hossain, K. Iimura, and T. Kato, Chem. Phys. Lett. **325**, 503 (2000).

[13] A. Gericke and H. Hühnerfuss, Thin Solid Films **245**, 74 (1994).