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Detection of the Phase Transition of Langmuir–Blodgett Films on a Quartz-Crystal Microbalance in an Aqueous Phase[1]

Yoshio Okahata,* Kazuhiko Kimura, and Katsuhiko Ariga

Contribution from the Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan. *Received April 10, 1989*

Abstract: The frequency of the quartz-crystal microbalance (QCM) deposited with Langmuir–Blodgett (LB) films was observed to increase abruptly at the phase transition temperature (T_c) from solid to liquid crystalline state of LB films in distilled water when the temperature was gradually raised. The frequency increase at the T_c was not observed in the air phase. The LB films were observed from the frequency changes to swell (mass increase and frequency decrease) with the water penetration in the interlayers near (just below) the T_c but not to swell both in the solid state (below the T_c) and in the liquid crystalline state (above the T_c) when in a water phase. The frequency increase at the T_c of LB films can be explained by the fact that the slipping behavior occurs between the swelled hydrophilic interlayers in the fluid liquid crystalline state of LB films at the T_c. The QCM is a useful tool to characterize LB films in the water phase.

Interests in Langmuir–Blodgett (LB) films are widespread, and formations of well-oriented ultrathin films by transferring monolayers from a water surface are well-known.[2,3] The characterization of LB multilayer films has been widely studied in the dry state by various methods such as FT-IR spectroscopy, X-ray diffraction analyses, ellipsometry, and X-ray photon electron spectroscopy.[4–7] Although studies of the stability or the behavior of LB films in a water phase are important for the application as a molecular chip and a model of biological membranes containing enzymes, the evaluation of LB films in connection with a water phase has not been fully explored. Quartz-crystal microbalances (QCMs) are known to provide very sensitive mass measuring devices because of the resonance frequency changes upon the deposition of a given mass on the QCM electrode.[9–13] Recently, we have observed, with use of the frequency change of the QCM as a substrate of LB films, that water is incorporated with lipid monolayers from a water phase during a transfer process and that the incorporated water gradually evaporates through the layers when exposed to air.[8] The orientation of LB films can be discussed from the amount of incorporated water and the evaporation speed of water. We have also observed from the frequency change that the outer monolayer of LB films partly flakes when the LB film-deposited QCM passes through the air–water interface.[1] The QCM is a useful tool to characterize LB films in air and water phases.[1,8,14] The fundamental principle in the above studies involves the frequency change due to the mass increase or decrease on the QCM by deposition or elimination.

In this paper, we report a new application of the QCM plate to detect the fluidity change from solid to liquid crystalline state of LB films on the quartz plate in that water phase. The frequency of the LB film-deposited QCM was observed to increase abruptly at the phase transition temperature (T_c) of LB films when the temperature was raised gradually in a water phase. The apparatus of frequency measurements of the LB film-deposited QCM and structures of LB film-forming amphiphiles are shown in Figure 1.

Experimental Section

Apparatus. The experimental apparatus comprised a 9 MHz, AT-cut quartz-crystal plate (0.568 cm^2) on each side of which the 0.20 cm^2 Ag electrode had been deposited and a homemade oscillator had been designed to drive the quartz at its resonance frequency.[8,13] The quartz-crystal microbalance (QCM) was driven at 5-V dc, and the frequency of the vibrating quartz was measured by an Iwatsu frequency counter (SC 7201 Model) attached to the microcomputer system (NEC, PC 8801 Model). The following equation has been obtained for the AT-cut shear mode QCM[12,15]

$$\Delta F = \frac{-2F_o^2}{A\sqrt{\rho_q\mu_q}}\Delta m \tag{1}$$

where ΔF is the measured frequency shift (Hz), F_o the parent frequency of QCM (9×10^6 Hz), Δm the mass change (g), A the electrode area (0.20 cm^2), ρ_q the density of quartz (2.65 g cm^{-3}), and μ_q the shear modulus (2.95×10^{11} dyne cm^{-2}). Calibration of the QCM used in our experiments showed that a frequency change of 1 Hz corresponded to a mass increase of 1.05 ± 0.01 ng on the electrode of QCM.[8,13]

$$\Delta m = -(1.05 \pm 0.01) \times 10^{-9}\Delta F \tag{2}$$

Materials. Ethyl octadecanoate ($C_{17}COOEt$) and octadecyl alcohol ($C_{18}OH$) were purchased as analytical grade chemicals. Preparations of 1,3-dioctadecyl-*rac*-glycero-2-ol ($2C_{18}OH$),[16] *N*,*N*-dioctadecylsuccinamic acid ($2C_{18}COOH$),[17] dioctadecyl glutamate HCl salt ($2C_{18}$-glu-NH_3^+),[18] trimethylammonium-type dioctadecyl glutamate ($2C_{18}$-glu-N^+3C_1),[18] and γ-(*N*,*N*-dioctadecylsuccinylamino)propyltriethoxysilane ($2C_{18}Si$)[17] were reported elsewhere. The purity of monolayer-forming amphiphiles was confirmed by thin-layer chromatography with a flame ionization detector (Iatron Laboratories Co., Tokyo, Model TF-10), NMR and IR spectroscopy, and elemental analysis (C, H, and N within ±0.2%).

Preparations of LB Films. Highly purified water by Milli-Q (Millipore Co. Ltd) was used as a subphase (18 MΩ cm). A benzene solution (0.8 mg mL^{-1}) of monolayer-forming amphiphiles was spread on a subphase in a Teflon-coated trough (475×150 mm^2) with a microprocessor-controlled Teflon barrier (San-Esu Keisoku Co., Fukuoka, Japan).[8,17] The monolayer was continuously compressed at the speed of 180 mm^2 s^{-1}, and surface pressure (π)–area (A) isotherms were stored automatically in a microcomputer at 20 °C. The QCM plate was lowered and raised at a speed of 5–100 mm min^{-1} through the monolayer on a subphase at 25–40 mN m^{-1}, and Y-type LB films (2–30 layers) were de-

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* Author to whom all correspondence should be addressed.

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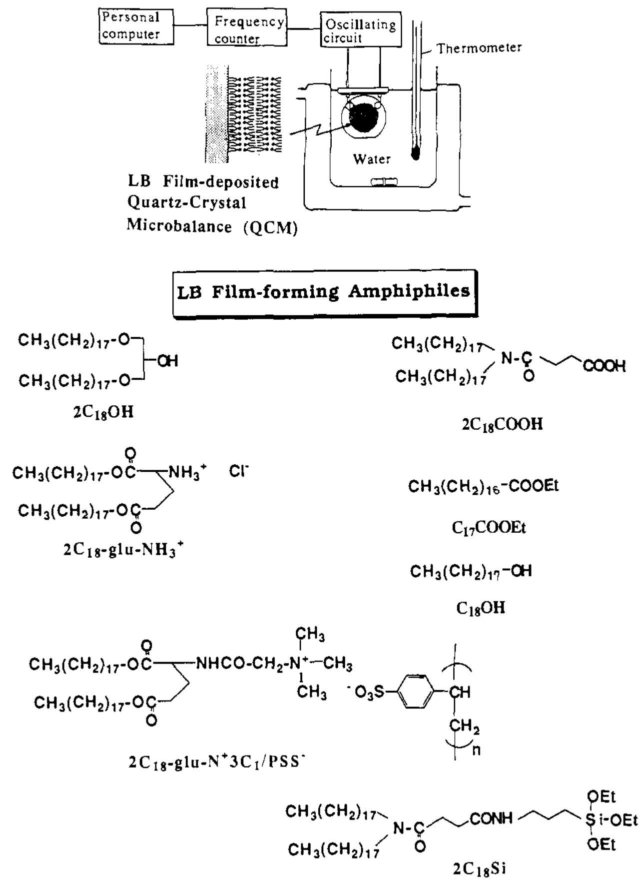

Figure 1. Apparatus of frequency measurements of LB film-deposited quartz-crystal microbalance (QCM) and structures of monolayer-forming amphiphiles.

posited on each side of the QCM plate. After drying in air, the deposited amount (a transfer ratio) of LB films was confirmed from the frequency decrease (mass increase) of QCM according to eq 2. When $2C_{18}OH$ monolayers were deposited with 10 layers on each side of QCM, the mass on the QCM electrode could be calculated to be 1023 ± 5 ng from the frequency decrease of 974 ± 5 Hz. This value was highly consistent with the theoretical mass of 20 dry monolayers of $2C_{18}OH$ (983 ng) calculated from the area per molecule in the monolayer (0.395 nm^2 at 40 mN m^{-1} from π-A isotherms) and the area of the QCM electrode (0.196 × 2 cm^2). Thus $2C_{18}OH$ monolayers could be deposited on the QCM with a transfer ratio of 1.02 ± 0.03. Other monolayer-forming amphiphiles ($C_{18}COOEt$, $C_{18}OH$, $2C_{18}COOH$, $2C_{18}$-glu-NH_3^+, polymeric $2C_{18}Si$, and $2C_{18}$-glu-N^+3C_1/PSS^-) were also confirmed to be deposited with a transfer ratio of 1.01 ± 0.02.

Frequency Measurements in Water. The LB film-deposited QCM was immersed in distilled water, and the frequency change was followed when the ambient temperature was raised and lowered gradually at the rate of 0.07–1.5 °C min^{-1}. In the swelling experiments, the frequency decrease was followed when the LB film-deposited QCM was immersed in distilled water at a constant temperature. Differential scanning calorimetry (DSC) of aqueous dispersion of monolayer-forming amphiphile crystals was carried out with a Daini-Seikosha Model SSC-560 instrument (an Ag sample pan, heating rate: 2 °C min^{-1} in the range of 5–90 °C). A sharp endothermic peak at the T_c could not be observed for the LB film (30–50 layers) deposited on the QCM plate because of the low sensitivity of DSC measurements.

Results and Discussion

Figure 2 shows the frequency changes of the QCM deposited with $2C_{18}OH$ LB films (30 layers on each side) when the ambient temperature was raised gradually. The frequency hardly changed when the LB film-deposited QCM was set in an air phase and the temperature was raised (curve a). The frequency of the naked QCM increased gradually with the rising temperature of the water because of the viscosity change of the water medium (curve b).[19,20]

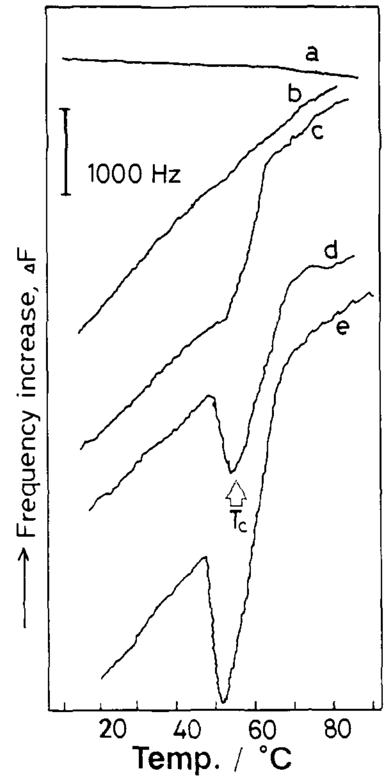

Figure 2. Frequency changes of the QCM deposited with $2C_{18}OH$ LB films (30 layers) on each side of the quartz when the ambient temperature was raised gradually in the air or water phase: (a) $2C_{18}OH$ LB films in air, (b) naked QCM in water, (c) $2C_{18}OH$ LB films in water at a rate of 1.5 °C min^{-1}, (d) $2C_{18}OH$ LB films in water at a rate of 0.4 °C min^{-1}, and (e) $2C_{18}OH$ LB films in water at a rate of 0.07 °C min^{-1}. The arrow shows the phase transition temperature (T_c) obtained from DSC measurements of the aqueous dispersion of $2C_{18}OH$ crystals.

The frequency abruptly increased near 53 °C in a water phase when the temperature was raised relatively fast (1.5 °C min^{-1}, curve c), which was consistent with the phase transition temperature (T_c) from solid to liquid crystalline state of aqueous dispersion of $2C_{18}OH$ crystals obtained from DSC measurements.

When the temperature was raised slowly, the frequency of the $2C_{18}OH$ LB film-deposited QCM decreased just below the T_c and then increased (curves c and d in Figure 2). The magnitude of the frequency decrease at the T_c increased with the decreasing of the temperature raising speed. The frequency decrease and the following increase near the T_c could be observed reproducibly when the temperature was raised again after cooling to room temperature several times. The mass of the LB film on the QCM was confirmed not to change when the frequency was measured in dry air before and after the temperature-change experiments in water. This indicates clearly that LB films on the QCM did not peel from the substrate during experiments even in the hot water, and the frequency decrease and the followed increase at the T_c are not explained by the mass change due to the peel of LB films from the substrate.

Figure 3 shows swelling behaviors of the $2C_{18}OH$ LB films on the QCM in the water phase. When the LB film-deposited QCM was immersed in water at 22 °C in the solid state of LB films, the frequency hardly changed (curve a). On the contrary, the frequency largely decreased and reached −3000 Hz corresponding to the mass increase of 3100 ng (103 wt % of 30 layers LB films) at 50 °C, just below T_c (curve b). At temperatures above T_c (at 60 °C), the frequency abruptly increased at first and then hardly changed with time (curve c). The abrupt frequency increase

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(20) The frequency change of 2500 Hz in the range 20–80 °C is very large and cannot be explained except by density-viscosity changes in water, which accounts for ca. 700 Hz. The frequency of the naked QCM in the water phase depends on other factors such as the depth of immersion, the length of the steel supporting wire, and so on.

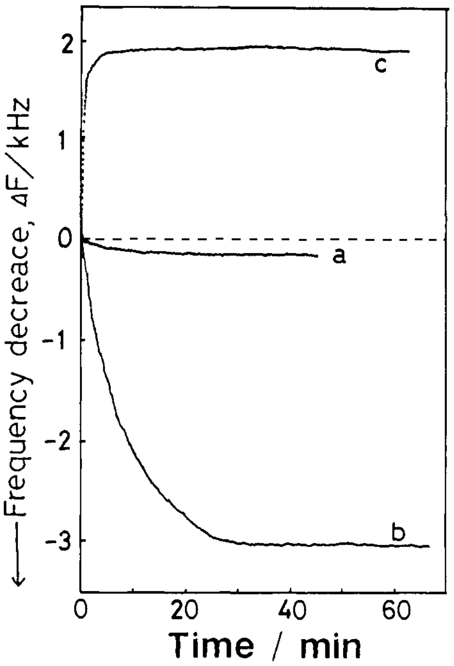

Figure 3. Swelling behavior of $2C_{18}OH$ LB films (30 layers) on the QCM in water at (a) 20 °C (below the T_c), (b) 50 °C (just below the T_c), and (c) 60 °C (above the T_c).

($\Delta\Delta F$) can be explained by curves c–e in Figure 2. When the QCM was exposed in air after these experiments, the frequency gradually increased (the mass decrease) and reverted to the original value, which means the evaporation of the water incorporated into interlayers of LB films in the water phase. Thus, the $2C_{18}OH$ LB films swelled largely when they evolved to the fluid liquid crystalline state near the T_c but not in the solid state below the T_c and the liquid crystalline state above the T_c. The frequency decrease just below the T_c when the temperature was raised slowly (curves d and e in Figure 2) can be explained by the swelling of LB films in the phase-separated (crystal–liquid crystal coexisted) state near the T_c. However, the large amount of swelling seems to not be important to cause the frequency increase at the T_c because the large $\Delta\Delta F$ value was observed even at the small amount of swelling.

Figure 4 shows the effect of the number of layers of $2C_{18}OH$ LB films on the QCM on the frequency increase at the $T_c(\Delta\Delta F)$. The $\Delta\Delta F$ values were plotted against the number of layers of LB films in Figure 4B. When less than 10 layers of $2C_{18}OH$ LB films were deposited on each side of the QCM, the frequency jump at T_c was hardly observed, and the $\Delta\Delta F$ increased linearly with the increasing of the layer number above 10 layers.

The frequencies of the QCM are known to decrease with the increasing of the mass deposited on the electrode in air phase.[8-13] The frequency decrease was measured at each time in the air phase and in the water phase at 20 and 60 °C when the $2C_{18}OH$ LB films were transferred on the QCM with each number of layers. Figure 5 shows the correlation between frequency decreases and the number of layers of $2C_{18}OH$ LB films deposited on the electrode both in air and water phases. In a water phase at temperatures below the T_c (at 20 °C), the frequency decreased linearly with the increasing of the layer number transferred on the QCM, and the slope (1.0 ± 0.1 ng/Hz) was highly consistent with eq 2 (1.05 ± 0.01 ng/Hz) as well as in the air phases (20–70 °C). This means that all mass of LB films on the QCM vibrates with the quartz plate in the solid state below T_c in a water phase and is independent whether in the solid or fluid state in the air phase. However, in the fluid liquid crystalline state above T_c (at 60 °C) in the water phase, the frequency hardly decreased with the increasing of the mass above 10 layers of LB films on each side of the QCM plate. This indicates that the upper layers of fluid LB films above 10 layers hardly vibrate with the QCM plate. This is also indicated in Figure 4: the $\Delta\Delta F$ value of n layers of LB films is consistent with the mass of (n–10) layers of LB films on the QCM.

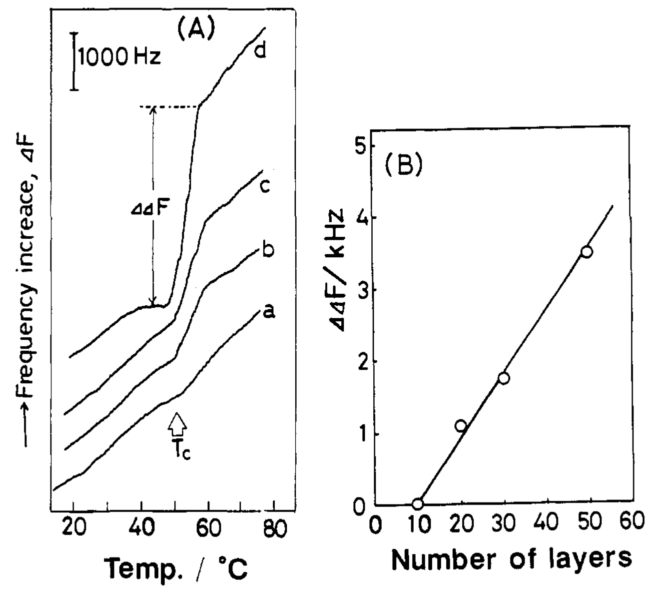

Figure 4. Effect of the number of layers of $2C_{18}OH$ LB films on the QCM on the frequency change at T_c ($\Delta\Delta F$) in the water phase (scan rate: 1.5 °C min^{-1}). LB films were deposited with (a) 10 layers, (b) 20 layers, (c) 30 layers, and (d) 50 layers on each side of the QCM plate.

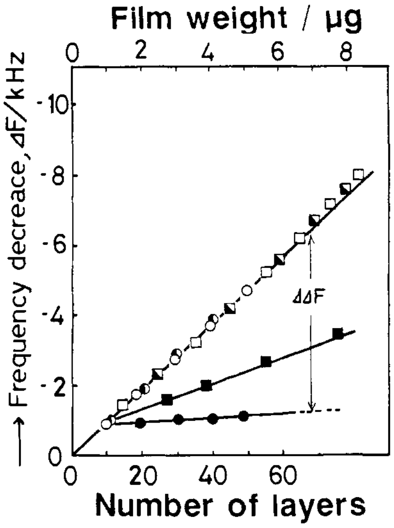

Figure 5. Correlation between frequency decreases of the QCM and the layer numbers of $2C_{18}OH$ LB films or the mass of the $2C_{18}OH$ cast film deposited on the QCM: (○) the LB film in air at 20–70 °C, (□) the cast film in air at 20–70 °C, (◐) the LB film in water at 20 °C (below T_c), (◧) the cast film in water at 20 °C (below T_c), (●) the LB film in water at 60 °C (above T_c), and (■) the cast film in water at 60 °C (above T_c).

Figure 6 shows frequency changes of 10 layers of the $2C_{18}OH$ LB films on the QCM in a water phase when the temperature was raised gradually at a different rate. The abrupt frequency increases at T_c were not observed in 10 layers of the LB films independent of the temperature raising speed, which agrees with the effect of the number of layers shown in Figures 4 and 5. When the temperature was raised slowly at 0.4 and 0.07 °C min^{-1}, the swelling behaviors were observed near the T_c, and the frequency reverted nearly to the base line above the T_c. This means that the incorporated (swelling) water at the T_c is unloaded completely though slowly at temperatures above the T_c as well as in the solid state below the T_c. Figure 7 shows swelling behaviors at different temperatures when the QCM deposited with 10 layers of $2C_{18}OH$ LB films was immersed in the water phase. The small amount (10 layers) of LB films on the QCM swelled slightly only near the T_c, and the frequency enhancement was not observed at 60 °C in the fluid state of LB films.

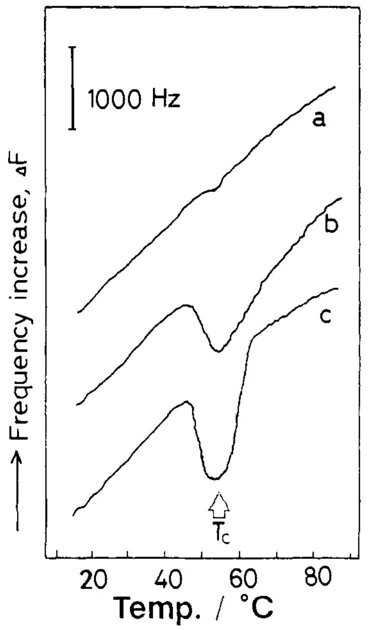

Figure 6. Frequency changes of the QCM deposited with 10 layers of the $2C_{18}OH$ LB films on each side when the temperature was raised at a rate of (a) 1.5, (b) 0.4, and (c) 0.07 °C min^{-1} in the water phase.

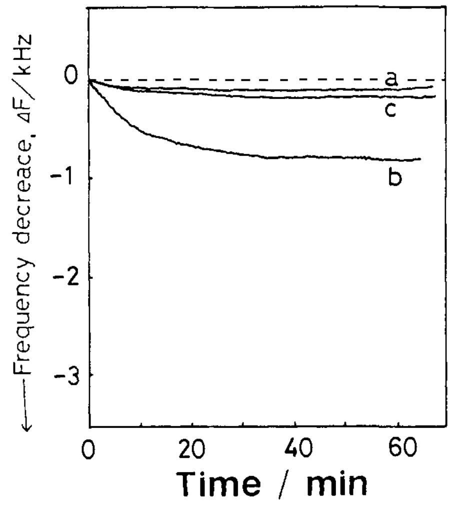

Figure 7. Swelling behavior of $2C_{18}OH$ LB films (10 layers) on the QCM in the water phase at (a) 20 °C (below the T_c), (b) 50 °C (just below the T_c), and (c) 60 °C (above the T_c).

From the findings of Figure 2–7, the frequency increase of the LB film-deposited QCM at T_c can be explained as follows. When LB films on the QCM become the fluid liquid crystalline state at T_c, water penetrates into hydrophilic interlayers, and the hydrated fluid LB films begin to slip between interlayers (do not vibrate with the quartz plate). As a result, the abrupt frequency increase at T_c of LB films is observed. Only a small amount of swelling is required for the slipping behavior because the magnitude of the frequency increase ($\Delta\Delta F$) was nearly independent of the swelling amount (see curves c–e in Figure 2). Swelling behavior at T_c is important to slip between interlayers because the frequency increase at T_c was not observed in the air phase.

The similar frequency changes at the phase transition were observed both in the air and water phases when the QCM covered with liquid crystal compounds such as *p*-(pentyloxy)-*p'*-cyanobiphenyl (PCB) showing a smectic phase at 43 °C, *N*-(*p*-ethoxybenzylidene)-*p'*-butylaniline (EBBA) showing a nematic phase at 36 °C, and cholesteryl dodecanoate (ChD) showing a chloesteric phase at 82 °C.[21] The magnitude of the frequency enhancement at the T_c of the smectic PCB-coated QCM was 2–5 times larger than those of the nematic EBBA- and cholesteric ChD-coated QCMs. This means that the multilayered structure of the smectic phase parallel to the QCM plate plays an important role in the frequency change at the T_c in addition to the fluidity or elasticity change from solid to nematic or cholesteric phase. These findings support the explanation that the frequency enhancement at the T_c of the LB film-deposited QCM is mainly due to the slipping behavior at swelled interlayers although the frequency is also affected slightly by the fluidity or elasticity change at the T_c.

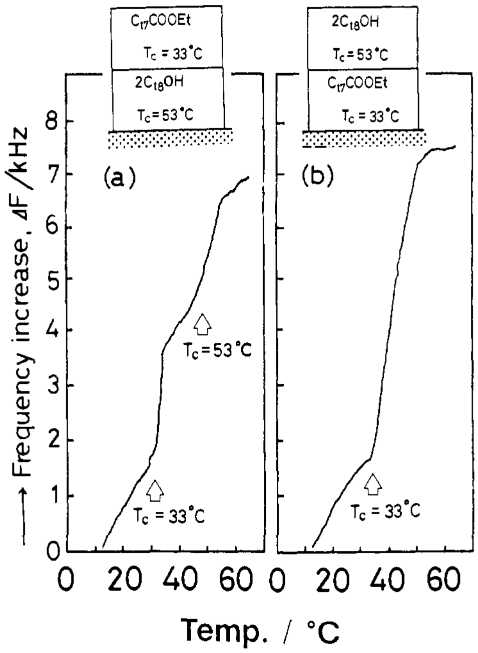

Figure 8. Frequency changes at the T_c of double-decker-type $2C_{18}OH/C_{17}COOEt$ LB films on the QCM in a water phase: (a) $C_{17}COOEt$ LB films (30 layers, T_c = 33 °C) were deposited on the $2C_{18}OH$ LB films (30 layers, T_c = 53 °C) on the QCM and (b) $2C_{18}OH$ LB films (30 layers) were deposited on the $C_{17}COOEt$ LB films (30 layers) on the QCM. The temperature was raised from 10 to 60 °C at a rate of 1.5 °C min^{-1}.

When a chloroform solution of $2C_{18}OH$ was cast on the QCM plate, the linear correlation according to eq 2 was observed in the air phase and at 20 °C (in the solid state below T_c) in the water phase as well as those of LB films (see Figure 5). In the fluid state above T_c (at 60 °C) in the water phase, however, the frequency decrease due to the mass deposition gradually increased with increasing the cast amount even above 0.8 μg (corresponding to the mass of 30 layers of LB films). Since the cast film forms the relatively disturbed multibilayer structures compared with LB films, the slipping behavior between interlayers seems to have difficulty in occurring in the fluid hydrated state.

Figure 8 shows the frequency change at T_c of $2C_{18}OH/C_{17}COOEt$ double-decker-type LB films on QCM when the temperature was raised gradually at a rate of 1.5 °C in water. When $C_{17}COOEt$ LB films (30 layers were deposited on the $2C_{18}OH$ LB films (30 layers) on the QCM plate, the frequency increases were observed at T_c at 33 °C for $C_{17}COOEt$ and 53 °C for $2C_{18}OH$ LB films, respectively. This means that the upper LB films of $C_{17}COOEt$ begin to slip at 33 °C, and then the lower $2C_{18}OH$ LB films slip at 53 °C in the fluid state. When the $2C_{18}OH$ LB films were deposited on the $C_{17}COOEt$ LB films, the frequency increase was observed only at 33 °C (T_c of the lower $C_{17}COOEt$ LB films). Thus, the slipping behavior of the upper LB films (T_c = 53 °C) is not detected since the lower LB films begin to slip and do not vibrate with the quartz plate above 33 °C.

The magnitude of the frequency changes at the respective T_c of other lipid LB films deposited on QCM in the water phase at the temperature raising speed of 1.5 °C min^{-1} is summarized in Table I. Monomeric LB films of dialkyl type $2C_{18}OH$,

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Table I. Frequency Changes of Lipid LB Films (30 layers) at the Phase Transition Temperature (T_c) on the QCM in a Water Phase[a]

LB films	T_c[b]/°C	$\Delta\Delta F$/Hz
$2C_{18}OH$	53	1800 ± 150
$2C_{18}COOH$	50	1500 ± 100
$2C_{18}$-glu-NH_3^+	52	1200 ± 100
$C_{18}OH$	55	1500 ± 100
$C_{17}COOEt$	33	1700 ± 100
$2C_{18}Si$[c]	44[e]	0
$2C_{18}$-glu-N^+3C_1/PSS^-[d]	45[e]	0

[a] Temperatures were raised at a rate of 1.5 °C min^{-1}. [b] The temperature where the frequency increased abruptly, which was consistent with T_c obtained from DSC measurements. [c] $2C_{18}Si$ monolayers were polymerized on the acidic subphase, and the polymeric monolayers were transferred on the QCM substrate. [d] $2C_{18}$-glu-N^+3C_1 monolayer was spread on the subphase containing PSS^- polyanions and transferred as the polyion complex LB films of $2C_{18}$-glu-N^+3C_1/PSS^-. [e] Obtained from DSC measurements.

$2C_{18}COOH$, and $2C_{18}$-glu-NH_3^+ and of monoalkyl type $C_{17}COOEt$ and $C_{18}OH$ showed the clear frequency increase at the respective T_c in the water phase ($\Delta\Delta F$ = 1200–1800 Hz). Thus, the swelling and slipping behaviors of LB films in the water phase due to the phase transition are general phenomena which can be detected from the frequency change of the QCM. However, when the cationic $2C_{18}$-glu-N^+3C_1 monolayer was spread on the subphase containing poly(styrenesulfonate) (PSS^-) polyanions and transferred as a polyion complex LB films of $2C_{18}$-glu-N^+3C_1/PSS^- on the QCM,[22] the frequency change was not observed at the respective T_c (45 °C obtained from DSC measurements). When γ-(*N,N*-dioctadecylsuccinylamino)propyltriethoxysilane ($2C_{18}Si$) is spread on the acidic aqueous solution, the $2C_{18}Si$ monolayer can be easily polymerized on the subphase with a Si–O–Si linkage and can be transferred as polymeric Y-type LB films covalently crosslinked between interlayers.[17] In the case of the polymeric $2C_{18}Si$ LB films deposited on the QCM, the frequency enhancement was not observed at T_c although a sharp endothermic peak was observed at 44 °C by DSC measurements of aqueous dispersion of polymeric $2C_{18}Si$ LB films. Since these LB films are polymerized with polymeric counter ions or Si–O–Si linkages between interlayers near the hydrophilic head groups, the slipping behavior (the frequency increase at T_c) is difficult to occur at the fluid state, although the melting of alkyl chains occurs at the respective T_c.

Summary

Although characterizations of LB films in aqueous solutions are difficult to study because of the limitations of measurement methods, the quartz-crystal microbalance (QCM) can detect directly that LB films do not peel from the substrate in the water phase and that the swelling and the slipping behaviors between interlayers occur in the fluid liquid crystalline state above T_c of LB films. The QCM is a useful tool to characterize the LB films in air and water phases. This is the first example to show that QCM can detect the fluidity change of coating well-oriented layered materials such as LB films in addition to the frequency change due to the mass increase on the electrode.

Registry No. $C_{17}COOEt$, 111-61-5; $C_{18}OH$, 112-92-5; $2C_{18}OH$, 18794-74-6; $2C_{18}COOH$, 37519-63-4; $2C_{18}$-glu-NH_3^+, 123726-22-7; $2C_{18}$-glu-N^+3C_1, 123726-24-9; $2C_{18}Si$, 105442-22-6.

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The Course of the Reaction of Azobenzene with Chromium Carbene Complexes

Louis S. Hegedus* and Bruce R. Lundmark

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

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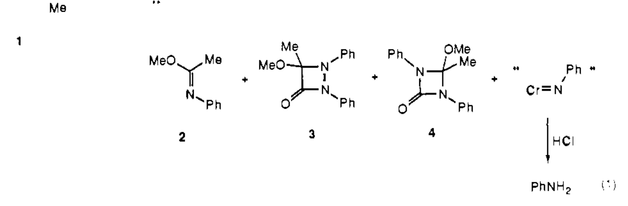
Abstract: The dark reaction between *cis*-azobenzene and pentacarbonyl[(methoxy)(methyl)carbene]chromium(0) was followed by ^1H NMR spectroscopy. The intervention of two discrete intermediates—thought to be a zwitterion and a metallacycle—was detected. Carrying out the reaction in hexane under a carbon monoxide atmosphere caused the reaction to stop at the metallacycle stage. Photolytic decomposition of this produced 1,3-diazetidinone and imidate products, as well as small amounts of azobenzene. 1,2-Diazetidinone products were thought to result from a primary photoreaction between *cis*-azobenzene and a photogenerated (methoxy)(methyl)ketene chromium complex.

Several years ago, an unusual photoreaction between azobenzene and chromium carbene complexes to produce metathesis products and cyclocarbonylation products (eq 1) was reported from these laboratories.[1] At that time, a mechanism involving a 2 + 2 photocycloaddition of the azobenzene to the carbene to give a diazachromacyclobutane, followed by fragmentation and/or CO insertion, was advanced. Subsequent studies have shown that photolysis of carbene complexes such as **1** promotes a reversible CO insertion into the chromium–carbene bond to produce a metal-bound ketene,[2] a process that cannot account for the products observed in eq 1. This prompted a careful investigation of this reaction, the results of which are reported below.



(1)

Results and Discussion

A mechanistic scheme for the reaction in eq 1 must accommodate the following observations. (1) The reaction between *trans*-azobenzene and the carbene complex **1** does *not* occur in

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(1) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263.

(2) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122.

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